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INFORMATION CONTAINED HEREIN IS PROPRIETARY FOR FOUR YEARS IN ACCORDANCE WITH FAR 52.227-20

High Performance Balloon Envelope Materials for Planetary Aerobots

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September 2002

Period Covered: 10/26/99 - 03/26/02

Final Report

Contract Number: NAS3-00026
Contract Amount: $599,956.00
Competitively Awarded
COTR: Mr. Constantino Rosca

Prepared for:

NASA Management Office/JPL
4800 Oak Grove Park
Pasadena, CA 91109-8099

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PROJECT SUMMARY

NASA has determined that Planetary Aerobots are one of the best lightweight vehicles for monitoring the atmosphere (in situ) and the surfaces (proximally) of the major planets of our solar system. Traditional aerobot/balloon envelope materials unfortunately cannot provide the required temperature capabilities and specific strength to meet the structural and weight goals for planned explorations such as those scheduled for Mars. In addition, traditional balloon envelope materials do not provide the desired durability and barrier properties to support long-term exploration.

Fortunately, a newly emerging material PBO (polybenzoxazole – a lyotropic liquid crystal polymer) has the potential to meet the property requirements for high performance planetary aerobot balloon envelope materials. Until recently, however, these high performance highly anisotropic polymers could not be processed into usable films that could be converted into balloon gores. The technology that has made PBO film a viable material has been pioneered by Foster-Miller, Inc. This technology utilizes innovative extrusion processes and extrusion dies to produce high strength and low permeability PBO films that exhibit in-plane isotropic properties. During a previous Phase I program, Foster-Miller demonstrated that PBO films can be developed to meet NASA's exacting specifications for an advanced planetary aerobot balloon envelope material that is lightweight, durable and capable of providing extended flight times over a wide range of temperatures (4°K to 700°K). This Phase I effort concentrated on improving the gauge uniformity of the extruded PBO film and developing processing protocols for producing high quality seams.

In this recently concluded Phase II program, Foster-Miller scaled up the process for extruding the PBO film to produce 22 in. wide film suitable for reduced scale aerobot balloon fabrication and a number of test balloons have been fabricated and tested by subcontractor, Raven Industries. These prototype balloons demonstrate that planetary aerobots fabricated from PBO film can meet or exceed NASA's rigorous requirements for an extraterrestrial balloon envelope material capable of extended missions on Mars or other similar bodies. These prototype balloons are being delivered to NASA for evaluation.

1. INTRODUCTION

This final report describes work conducted by Foster-Miller, Inc. under Contract No. NAS 3-00026 as part of a Phase II Small Business Innovation Research (SBIR) program monitored by NASA/Jet Propulsion Laboratory (JPL). The overall goal of this program was to develop fully functional, reduced scale planetary aerobot balloons for the Martian environment from Foster-Miller's PBO films. The high strength, low permeation rates, and high/low temperature capabilities of PBO film and seams were demonstrated during Phase I of this program. This Phase II program addressed the need to scale-up the extrusion process by a factor of 2 to produce continuous lengths of 21 in. wide PBO film with 10 percent (or less) thickness variation by designing and fabricating a new and larger counter-rotating die (CRD). During Phase I, we demonstrated that our CRD system can be modified to produce film with better gauge uniformity; however, this system was not capable of extruding PBO tubes larger than 9.0 in. wide (i.e., 3.0 in. in diameter). A newly designed CRD with larger diameter (larger width capabilities) was designed and fabricated in this Phase II program. In addition, the seaming technology utilized resulted in the translation of mechanical properties to those of the PBO film. Processing protocols for fabricating 100 in. seams for production evaluation and PBO balloons were developed based on experience gained during the fabrication of Venusian and Martian PBO Balloon seams, respectively. Reduced scale Martian balloons of 1.5m diameter were fabricated by subcontractor Raven Industries and are being delivered to NASA for evaluation.

1.1 Phase II Accomplishments

Specific Phase II objectives and accomplishments are summarized in Table 1.

Table 1. Technical objectives planned versus accomplished during Phase II

Planned: Produce high quality PBO film (≤10 percent thickness variation) using a scaled up (2X) custom CRD which incorporates new design features focused at reducing the radial runout of the rotating mandrels. Foster-Miller will enhance the diameter consistency of our PBO film and use improved weeping rings during extrusion to ensure the production of lay-flat film.

Accomplished: Produced ≈ 22 in. wide (7 in. diameter) lay flat film of acceptable quality for Martian aerobot balloon fabrication. Gauge variation on this wider film was still greater than 10 percent averaging 19.7 percent deviation on a thin film of 0.271 mil thickness. Raven Industries found this film to be acceptable for balloon fabrication.

Planned: Demonstrate the high strength of PBO film (extruded through the new CRD) at the high and low temperature extremes of the selected planetary atmosphere. Data obtained in this program will be combined with results obtained at JPL to show that these films can withstand the temperature extremes experienced during interplanetary travel.

Accomplished: 22 in. wide PBO films were tested for mechanical properties in both the machine and transverse directions at temperatures of 77°K and 295°K. Both modulus and tensile in both MD and TD and exceeded target values by 20 percent.

Planned: Construct and test balloon seams (~100 in. long) that exhibit the necessary durability and barrier properties for the intended destination planet.

Accomplished: Seams were fabricated and tested using Raven's commercial sealing technology. These seams were tested by Raven and met the adhesion and durability requirements. Differential pressure testing of a seamed film cylinder showed capability >4 psi as compared to a target value 0.0145 psi.

Planned: Design and construct lightweight, robust end-fittings and shock cords that can survive the rigors of this application without compromising sealing ability. Proper end-fitting design will enhance the performance of the balloon significantly; preliminary designs were produced during Phase I.

Accomplished: End fittings were designed and fabricated by Raven. These fittings met all test criteria for the spherical balloons fabricated during Phase II. Shock cords were not required for the specified spherical balloon.

Planned: Select a coating process for metallizing PBO balloon panels for UV radiation protection and demonstrate the ability of this appropriate PBO coating to survive packaging and deployment during a mission to Mars.

Accomplished: Plasma enhanced chemical vapor deposition (PECVD) of silicon oxide and fluorocarbon coatings developed by MetroLine Industries were evaluated for UV protection. Very thin films of both coatings provided better than 85 percent retention of mechanical properties after 32 days exposure to 340 nm UV radiation.

Planned: Construct and flight test model PBO balloon prototypes and evaluate the performance of each. These balloons will be delivered to NASA for further evaluation.

Accomplished: Two 1.5m diameter balloons were fabricated and static tested by Raven Industries and are to be delivered to NASA during the second week of May 2002. According to NASA only 10m and larger balloons can be flight-tested.

Planned: Prepare finalized designs and construction protocols for full-scale, functional Martian balloons.

Accomplished: Full-scale 10m diameter balloons will require a significant scale up (factor of 3X+) of the PBO film producing equipment to produce film of a sufficient width to avoid excessive seaming. Die runout (film thickness variation) could become extremely difficult for films of these widths.

The above objectives were structured to answer the following questions, which are paramount in establishing the performance of our proposed technology.

Table 1. Technical objectives planned versus accomplished during Phase II (continued)

Q: Can high quality PBO film (<10 percent gauge variation) be extruded using a newly designed, larger CRD suitable for commercial production of wider lay flat film?

A: High quality film meeting the performance specifications for the Martian balloons was produced using the larger CRD. Although thickness variations were still about 19 percent with this new die, the film was acceptable to Raven for fabrication of the 1.5m diameter prototype balloons.

Q: Does the PBO film extruded through the new, larger diameter CRD system meet all of the requirements for a Martian balloon envelope material?

A: Yes, with the possible exception of gauge variation.

Q: Can long PBO seams be constructed that exhibit similar characteristics of the PBO film itself? Will these seams retain the necessary mechanical and barrier properties after flexing and folding?

A: Raven fabricated and tested long seams on the PBO film that met the performance specifications for the Martian balloon material.

Q: Can the UV resistance of PBO be enhanced through the use of UV inhibitors and/or metallic coatings? Will these coatings remain on the PBO film throughout the duration of the mission?

A: Silicon oxide and fluorocarbon thin film coatings showed reasonable UV protection –85 percent retention of original properties under extended UV exposure- for the PBO film. No durability tests were performed under simulated Martian mission conditions.

Q: Can Martian PBO balloons be fabricated using improved end-fitting designs and construction techniques? Do these PBO balloons meet the performance requirements for an intended mission to Mars?

A: Two reduced scale Martian balloons of 1.5m diameter were fabricated and bench tested by Raven. All test data indicates that these balloons should meet the performance requirements for an intended mission to Mars.

2. BACKGROUND

2.1 Justification for Research

Comprehensive in situ research of the extraterrestrial atmospheres of Mars, Venus, Titan, and outer planets has been an elusive goal that has perplexed both NASA and the Russian Space Program for numerous years. Since 1960, Russia and the United States have manufactured 27 probes for Martian study; recently, the Mars Pathfinder mission (USA) was successfully carried out as part of NASA's low-cost Discovery series. Most probes simply drop through the atmosphere gathering data at descending altitudes until they land roughly 1 hr after deployment. This allows limited time for data collection. Probes attached to atmospheric balloons collect data for longer time periods, but operate at a relatively fixed altitude. These limitations have hindered scientific endeavors to better understand the atmosphere surrounding the planets of our solar system. A balloon with sustained flight capabilities and ability to traverse over a wide range of altitudes will provide NASA with an extremely flexible research tool for thoroughly analyzing various extraterrestrial atmospheres. For this reason, a new series of miniature robotic balloons are emerging as an important tool for next generation terrestrial climate investigation. Innovative balloon envelope materials are needed to support the development and implementation of high technology payloads carried by reversible fluid, zero-pressure, and super pressure robotic balloons. Foster-Miller's biaxially-oriented PBO films (i.e., in-plane isotropic films) are one of the most promising light weight, impermeable and high strength materials for meeting the demanding needs for extraterrestrial aerobot balloons.

2.2 Why Study Extraterrestrial Atmospheres?

Humankind has much to learn from other planets/moons in our solar system. Through the years, NASA has identified celestial bodies of key interest for planetary exploration, these bodies include Mars, Venus, Titan, and Jupiter. NASA's interest in these bodies cannot be fully summarized in this report, however, since missions to Mars are on the horizon, the following sections will briefly describe some aspects of Martian exploration.

Mar has many similar traits to Earth, and is often considered a little brother of Earth. Mars is an inhospitable world by Earth standards, but it is the best alternative home for life in our solar system. Although largely a frigid world, Mars does host balmy temperatures as high as 80°F on the equator. Water, so fundamental for the existence of life, is also present in the form of ice caps. The atmosphere is scarce. Surface pressure is presently about 7 mbar (Earth's is 1000). Table 2 compares the general characteristics of both planets. These traits include sidereal rotation periods, thin atmospheres, and roughly equivalent mean surface temperatures. The countless mysteries surrounding Mars has spawned the fabrication of many probes designed to give humankind insight to the wonders of this planet.

Table 2. General characteristics of Earth and Mars show many similarities

	Mars	Earth	Ratio (Mars/Earth)
Bulk Parameters			
Mass (10** 24 Kg)	0.6419	5.975	0.107
Equatorial Radius (Km)	3393	6378	0.532
Polar Radius (Km)	3373	6356	0.531
Core Radius (Km)	1700	3485	0.488
Ellipticity	0.0065	0.0034	1.912
Mean Density (Kg/m**3)	3933	5520	0.713
Surface Gravity (m/s**2)	3.69	9.78	0.377
Escape Velocity (Km/s)	5.03	11.19	0.450
Visual Geometric Albedo	0.15	0.38	0.395
Visual Magnitude V (1,0)	-1.52	-3.86	-
Solar Irradiance (W/m**2)	595	1380	0.431
Black-Body Temperature (K)	217	248	0.875
Topographic Range (Km)	36	20	1.800
Moment of Inertia	0.366	0.3308	1.106
Atmospheric Data			
Mean Surface Temperature (K)	210	288	0.73
Mean Surface Pressure (mbar)	6.9-9	1000	0.01
Orbital Parameters			
Semimajor Axis (10**6 Km)	227.9	149.6	1.524
Revolution Period (Days)	686.980	365.256	1.881
Sidereal Orbit Period (Days)	686.930	365.242	1.881
Synodic Period (Days)	779.94	-	-
Mean Orbital Velocity (Km/s)	24.13	29.79	0.810
Orbit Inclination (deg)	1.85	0.00	-
Orbit Eccentricity	0.0934	0.0167	5.593
Sidereal Rotation Period (hr)	24.6229	23.9345	1.029
Equatorial Inclination (deg)	23.98	23.44	1.023

2.3 Planetary Aerobot Technology

NASA's Planetary Aerobot Technology (PAT) involves the development of autonomous flying, robotic aerovehicles in the atmosphere of Mars, Venus, Titan and the outer planets. An aerobot is capable of one or more of the following activities: 1) autonomous state determinations; 2) periodic altitude variations where altitude, amplitude and period are design variables; 3) planetary winds; and 4) landing at a designated surface location. The PAT system will overcome the deficiencies such as limited data collection and incomplete atmospheric characterization that was difficult to accomplish in past atmospheric probes. These aerobots employ a reversible fluid balloon system that includes activation fluid reservoirs, heat exchangers valves that control the rate of fluid boil-off and condensation. As aerobot approaches the warmer surface of the planet the fluid boils-off, filling the balloon with gas and providing lift. As it ascends into cooler regions of the atmosphere, the lifting gas condenses back to a liquid, causing the balloon to descend. If descent closer to the planet surface is desired, a valve can be closed to prevent the boiled off liquid from escaping into the balloon envelope.

2.4 Advanced Lyotropic PBO Film Enduring the Extraterrestrial Environments

The frigid atmosphere of Mars demands a top performing organic material. Temperature extremes on Mars range from 145K up to about 310K. Temperature extremes on Titan range from 72K to 94K. The balloon materials for the low-altitude excursions over Mars, planned to take place in 2003 to 2005, will have to endure thermal cycling, high balloon pressure (2 to 4 mbar), radiation, and expansion after a nine-month packing time. In addition, the balloon and its seams must retain superb strength and barrier properties through the duration of the mission. Stress concentration must be minimized to prevent tearing and cracking. Foster-Miller has demonstrated that a new class of high performance polymer will endure these conditions better than other known organic materials such as Mylar or Teflon. Foster-Miller's PBO films have the durability, high specific strength, high barrier properties and dimensional stability to make extended Martian or Titan balloon flight possible.

The high tensile strength and low density of PBO film and fiber results in considerable weight savings when compared to other nonmetallic materials. Table 3 compares the specific strength and maximum operating temperature of Foster-Miller's biaxially-oriented PBO film and PBO fiber to other polymer films and fibers. The Teflon balloons that were used during the Vega Mission were 3.4m in diameter and weighed 12.5 kg. A PBO balloon of the same size and similar total lift capacity would weigh only 0.5 to 1.0 kg. For this upcoming mission to Mars, the balloon dimensions are to be 10 to 12m wide and 15 to 16m high but the total allowable weight of the compacted balloon must not exceed 10 kg. The high strength of Foster-Miller's PBO film (120 ksi tensile in machine direction) will allow the use of thinner films (about 0.25 mil thick) while still having the ability to contain a pressurized volume of gas. The area mass requirement for the balloon is 8 to 12 g/m^2. The area mass of 0.25 mil PBO film is calculated at 0.01 g/m^2 and 0.02 g/m^2 for 0.5 mil film. The weight savings could be used to carry additional monitoring equipment or batteries.

A month long balloon flight will require that very little of the internal gas (helium or hydrogen in this case) is lost due to permeation through the balloon walls. Foster-Miller's unique polymer extrusion process results in a PBO film with extremely low permeability.

Table 3. PBO film outperforms other polymer materials

Material	Specific Strength (in.) Film	Specific Strength (in.) Fiber	Maximum Working Temperature (°C)
PBO	68.8	495 to 516	500
Teflon	1.5 to 4.0	16 to 30 (TFE)	260
HDPE	4.5 to 5.9	519	80 to 120
Kapton	9.6 to 20.6	-	250 to 320
Upilex R	34.3	-	270
Upilex S	64.8	-	290
Kevlar	-	392 to 458	180
Spectra 1000	-	602	147
Vectran HS	-	345 to 432	110
Nomex	-	93	310

Figure 1 compares the extremely low permeability of Foster-Miller's PBO film to other polymer films. As seen, PBO is orders of magnitude lower in helium permeability than most other barrier polymers. Maintaining the lift capacity of the balloon is critical for an extended flight duration Martian atmospheric probe.

2.5 Foster-Miller's PBO Film Extrusion Technology

2.5.1 Description of PBO

PBO is a conjugated aromatic heterocyclic liquid crystalline polymer (LCP) with a chemical structure as shown in Figure 2. These materials have a high degree of molecular self-alignment due to the rigid-rod nature of the polymer repeat unit. This rigid-rod molecular structure results in a microscopic self-reinforced material with strength and stiffness of a composite, but without the matrix and fiber-matrix interface problems. Figure 3 shows the microstructure in expanded form compared to the size of reinforcing fibers used in composites. The finer scale of PBO reinforcement results in thinner, tougher and more dimensionally stable structures than can be made with fiber reinforced composites.

The synthesis of PBO results in a polymer solution that is 15 percent (by weight) PBO and 85 percent polyphosphoric acid. This is not a typical solution, but rather, an extremely high viscosity material. The neat polymer has no melting point or glass transition temperature hence must be processed in solution, and thus is classified as a lyotropic liquid crystal polymer. In addition to being an excellent structural material, PBO is highly resistant to corrosive chemicals.

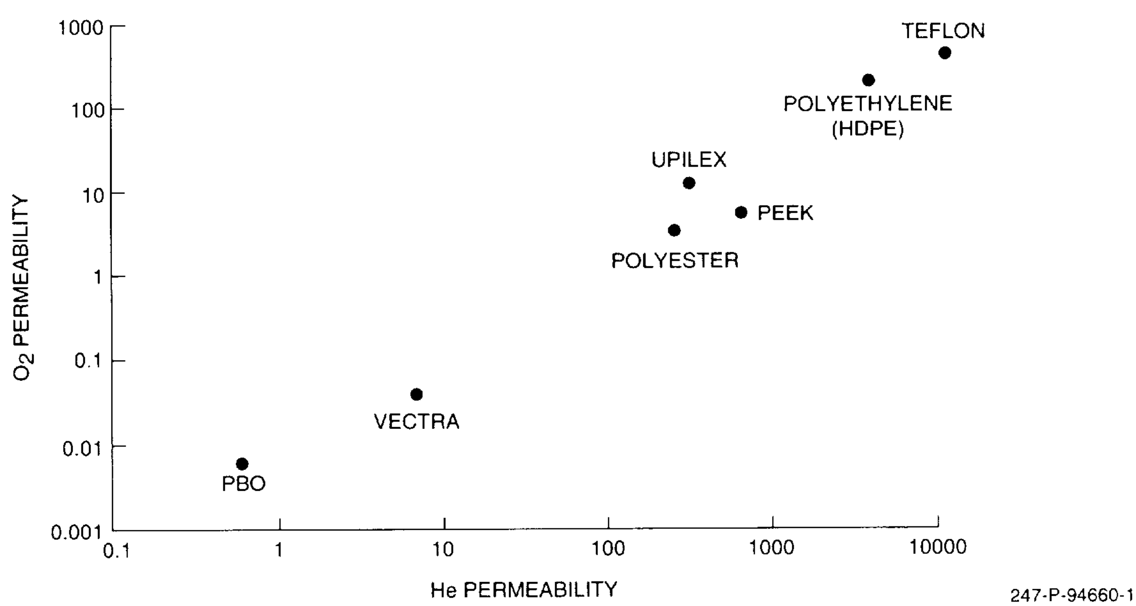

Figure 1. PBO permeability

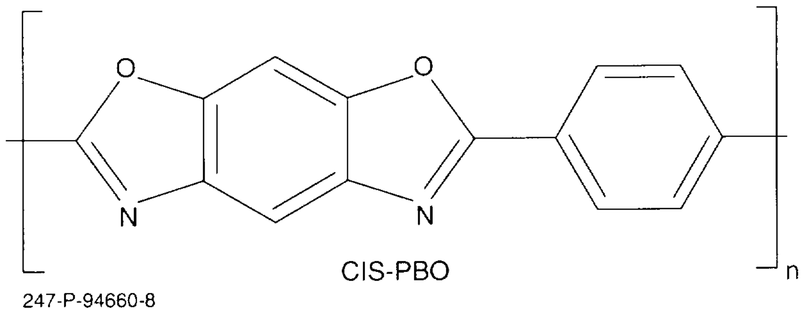

Figure 2. Chemical structure of PBO

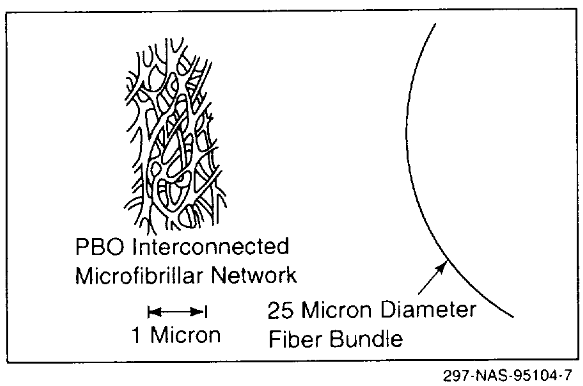

Figure 3. Microstructure of PBO

PBO's chemical resistance is for the most part due to its highly stable aromatic heterocyclic molecular structure. This polymer has been synthesized so that its electronic conjugation minimizes internal energy and produces exceptionally strong chemical bonds. The energy needed to break these bonds (the principal failure mechanism of corrosion) is significantly higher than most oxidizing agents.

2.5.2 Extrusion of PBO Film

When processed with conventional film extrusion dies, films produced from rigid-rod polymers like PBO have uniaxial fibrillar orientation that results in little or no transverse strength. Thus, with conventional processing techniques, their potential application is typically limited to highly reinforced tapes.

In response to this limitation, Foster-Miller has developed technology for producing biaxially-oriented film. Biaxial films (shown in Figure 4) have a molecular orientation of $\pm\theta$ from the machine (extrusion) direction. Unlike uniaxial films, Foster-Miller's biaxial films exhibit strength in the machine (MD), transverse (TD), as well as any other in-plane direction. These films can be tailored for different applications simply by controlling the angle θ to provide relatively isotropic in-plane properties if θ is 45 deg, or more highly uniaxial properties if θ is less than about 10 deg.

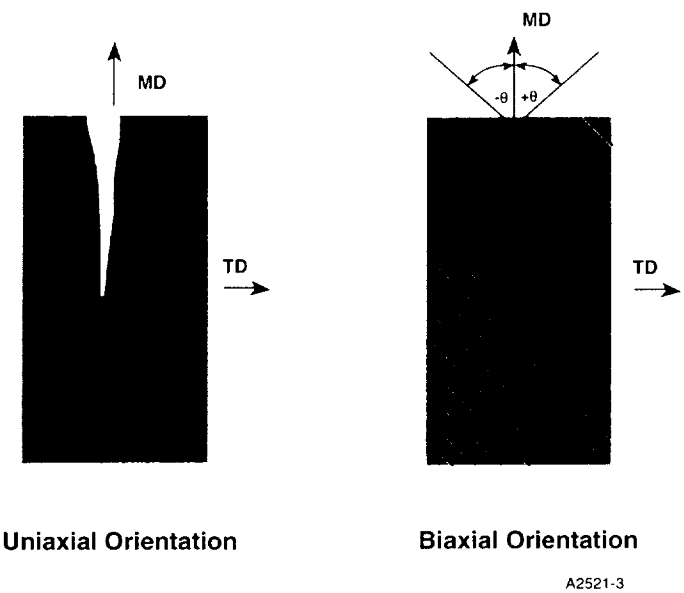

Figure 4. The effect of uniaxial versus biaxial orientation in ordered polymer films

Foster-Miller in the past has produced unique LCP films using a first generation die (counter-rotating die (CRD)) that was designed to eliminate many of the common problems associated with standard film extrusion of anisotropic rigid-rod polymers. This technological breakthrough resulted in films that exhibited major improvements in mechanical properties. Many engineering/application programs have been successfully completed using PBO films that were produced using our CRD. In fact, feasibility studies conducted during Phase I of this program utilized PBO film extruded through our CRD.

The CRD (Figure 5) uses two annular and concentric mandrels that rotate in opposite directions. The rotation of the mandrels creates a transverse shear flow that is superimposed on the axial shear developed as the polymer melt is extruded through the die. The angle that the LCP fibrils make with the longitudinal axis of the tubular extrudate is $\pm\theta$, where θ can be varied from near-zero to about 60 deg. The die rotation presets the biaxial ($\pm\theta$) orientation of the emerging extrudate. Subsequent post-die blow (radial expansion) and draw (extrusion direction stretching) is used to further adjust and enhance the biaxial orientation.

The tubular extrudate leaving the CRD is expanded radially (blown) with pressurized nitrogen and stretched in the machine direction by pinch rolls to achieve the desired film thickness. The PBO parison passes through an aluminum "water seeping weeping ring" that controls bubble diameter and provides a cushion of water to minimize film surface imperfections. The blown and drawn PBO bubble is immediately quenched in a water bath where the film structure is coagulated "locked in place" and the polyphosphoric acid is hydrolyzed into phosphoric acid. The PBO film is collected under water on a spool that is later transferred to a fresh water storage tank where residual acid is removed from the film. This process is illustrated in Figure 6.

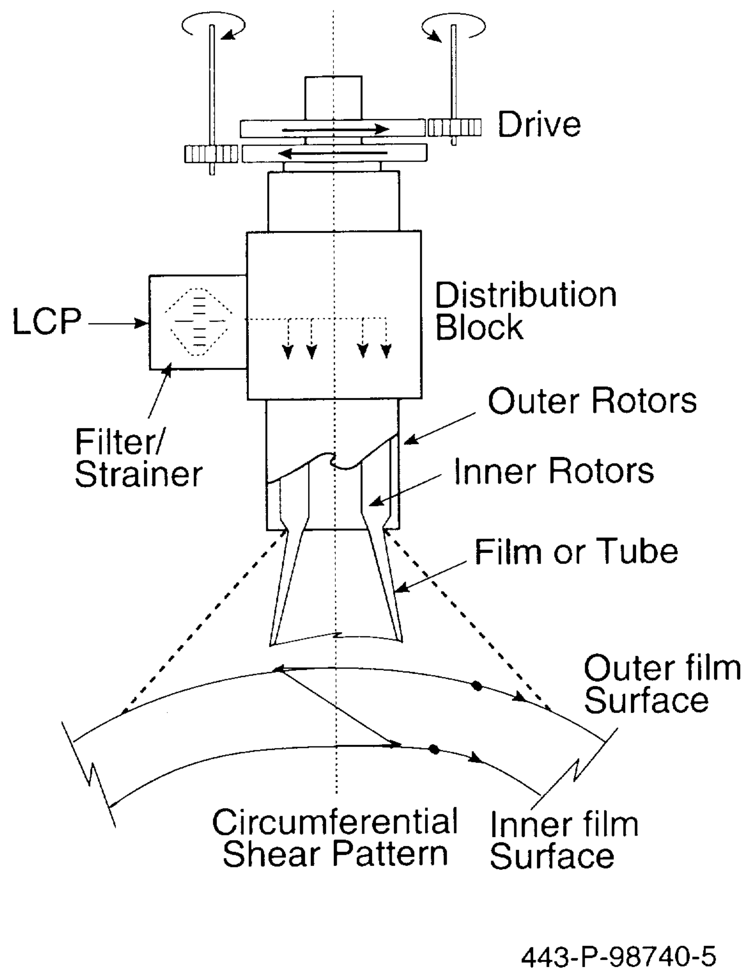

Figure 5. Foster-Miller's counter-rotating die

Before the extruded PBO film can be used it must be washed to remove all residual phosphoric acid and dried to remove all water. Most of the PBO produced with Foster-Miller's rotating dies is washed in tube form. Our PBO film washing system utilizes heated water tanks approximately 99 in. long with deionized (DI) water to wash both the inside and outside of our PBO film tubes. The washing system circulates warm water within the bath at a rate of 120 gal/hr, and replaces the washing water at a rate of 30 gal/hr. The washing system also has continuous temperature and pH monitoring capabilities. During the washing of a typical batch of PBO film the wash water temperature varies between 95 to 110°F, the wash water pH ranges from 2.5 to 7.0 and the washing cycle usually takes approximately 6 hr.

2.5.3 Post Extrusion Processing of PBO Film

Coagulated, water-swollen PBO film is dried under axial and hoop tension using a slow ramp and soak drying cycle. Axial and circumferential (or hoop tension) is respectively achieved using a combination of metal bellows and internal gas pressure. By adjusting these variables, the ultimate properties of the PBO film can be tailored to meet specific needs. The film properties most readily tuned by our drying process are: modulus, percent elongation, and tensile strength.

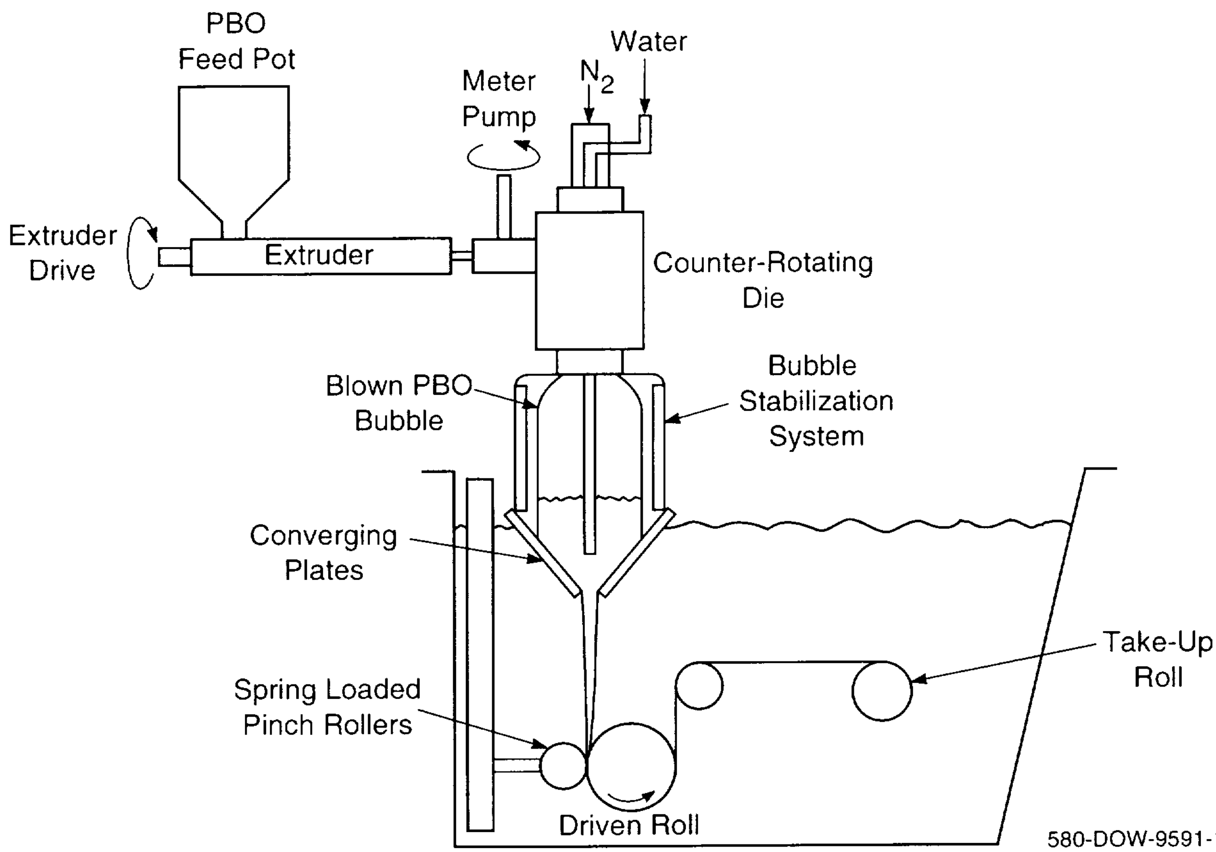

Figure 6. Lyotropic LCP film processing system

The relationship between drying tension and film properties is quite simple; as tension is increased, the percent molecular alignment retained in the PBO film is increased, this in turn, translates into higher modulus, higher tensile strength, and lower elongation.

Foster-Miller owns and operates two ovens for drying PBO film; a 3 ft long horizontal IR radiant oven for drying 3 in. diameter film tubes and a 9 ft long vertical convection oven for drying the 7 in. diameter film tubes produced during this Phase II program. PBO film adhesive bonding studies conducted on an earlier program indicated that the type of heating source can alter the surface energy and hence the bondability of the PBO film.

3. PHASE II WORK PERFORMED

Foster-Miller conducted this Phase II effort in a series of seven well-defined tasks:

- Task 1 - Define Material and Balloon Requirements.
- Task 2 – Scale-Up Production of PBO Film.
- Task 3 - Post Processing PBO Film.
- Task 4 – Develop Prototype PBO Seams Joining Techniques.
- Task 5 - Test PBO Film and Prototype Seams.
- Task 6 - Demonstrate Martian Environmental Compatibility.
- Task 7 – Fabricate Prototype Martian Balloons.

The work performed in each task is described below.

3.1 Task 1 – Determine Material Requirements

PBO film exhibits the strength, barrier properties, and thermal stability that make it a viable candidate for interplanetary balloon applications. However, the specific film thickness, diameter consistency ("flatness" of film), and orientation need to be well defined if a Martian balloon is to be constructed. Past balloon design analysis reveal that a 0.25 mil film is ideal for a low pressure, aerobot balloon. In practice, the relatively high thickness variation of most of our PBO films coupled with the difficulty of balancing thin PBO film properties forced the use of thicker films. A large portion of this Phase II program was dedicated to the fabrication of new and improved processing equipment capable of producing film to meet targets for quality. These targets were:

1. Film thickness variation of ≤10 percent.
2. Diameter consistency of ≤0.5 percent.
3. Minimum PBO thickness of 0.236 mil (6μ).
4. Axial and transverse tensile properties balanced within 15 percent.

Based on these established targets, PBO film with a nominal thickness of 0.3 mil (based on 20 percent deviation to maintain 0.24 mil target thickness) and a fibril orientation of ±22 deg was determined to meet the requirements of the program. Although the mechanical properties will not be balanced at ±22 deg orientation, they will be sufficient to meet the strength requirements of the program.

Raven Industries (Sulphur Springs, TX) was subcontracted to provide the PBO balloon design and analysis and fabricate four balloons. Specifications for the model and flight balloons constructed during this program are presented in Table 4. The design and analysis required that

Table 4. Specifications for Phase II PBO balloons

Quantity	Model Balloon 2	Flight Balloon 2
Purpose	Evaluate integrity of end fittings and structural components during pressurized tests. High density packing tests. Results will be used to determine volume requirements for Mars mission spacecraft	Dynamic evaluations in Earth atmosphere (JPL)
Balloon Geometry	Sphere	Sphere
Payload Capacity	<0.5 kg	1 kg
Balloon Diameter	1 m	1.5 m
Operating Pressure	1 mb	1 mb
Altitude	N/A	TBD
Design Stress on PBO Film	Tested to breaking stress	~79.3 MPa (11,500 psi) (131 MPa (19,000 psi) on full scale)

the thermal properties of the PBO film be measured. Properties that were measured included visible and infrared absorptivity and emissivity. UV resistance of PBO film was measured as a function of the retention of mechanical properties.

3.2 Task 2 – Scale-Up Production of PBO Film

Scale-up production of PBO film involved changes to three major aspects of the extrusion system. A new die design, a new vertical take-up assembly, and new extruder and barrel were required to produce the ultra thin uniform gauge PBO film.

3.2.1 New Die Design

A new die design was required to produce a 7 in. diameter film with Foster-Miller's counter-rotating die technology. The standard counter-rotating die mandrels were approximately 2.0 in. in diameter, which would result in a blow-up ratio of 3.5 to produce a 7 in. diameter bubble. Large blow-up ratios tend to cause problems with bubble stability, gage uniformity and are difficult to process continuously. Based on previous experience with 3 in. diameter extrusions, a 1.5 to 2.0 blow-up ratio was thought to be ideal thus a new die concept was designed (die assembly shown in Figure 7). The major hurdle was increasing the die mandrel diameter from 1.25 in. up to 3.5 in. required to produce film with a blow up ratio of 2. In addition to the new die adapters, several other modifications were incorporated to improve the quality of the extruded films. These ancillary modifications included:

- Addition of two bearium disks to hold screens packs to help filter and homogenize the polymer flow. The disks also doubled as a bearing to help control concentricity of the die

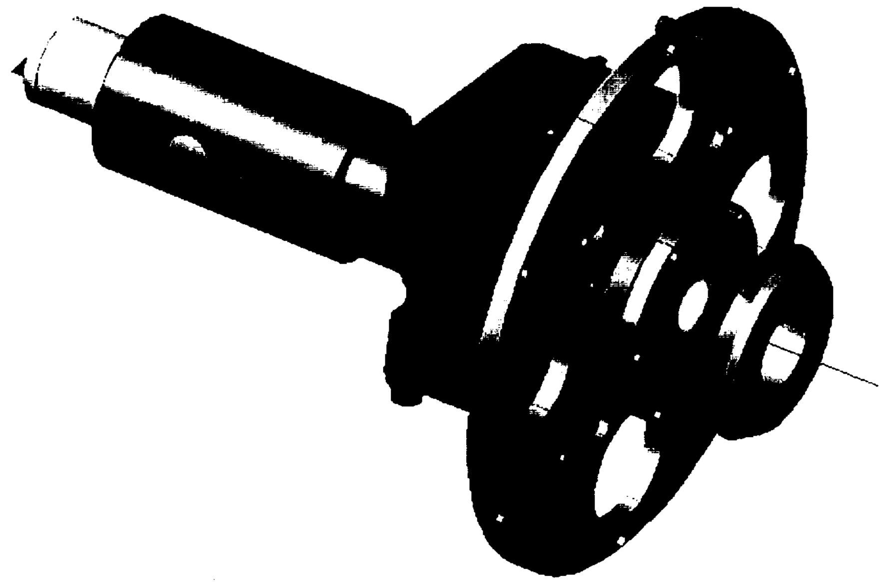

Figure 7. New die design concept

mandrels and adapters. Various screen pack configurations were used without any significant benefit to the visual overall quality of the extruded films.

- Homogenization of the PBO with the twin-screw extruder to eliminate the potential of the dope not being homogenous. Again, there was no discernable difference between films extruded from the "as received" dope and homogenized dope.

The first major change to the counter-rotating die design was the incorporation of a "trumpet-style" die adapter set as shown in Figure 8. The rational for its use was to allow the polymer to begin its flow in an outward direction to reach its final dimension. By radially accelerating the polymer outward within the die, lower pressures would be required to expand the film bubble to its final diameter. This in turn was thought to minimize the bubble instability caused by the rotation of the mandrels. Several modifications were made to the original concept as shown in Figure 7 to try to improve the overall surface quality of the blown film. These modifications, reasons for the changes and results of each are summarized briefly below.

- Undercut the adapter face to prevent the extruded PBO film from sticking to the chamfered cut and continues rotating with the inner mandrel well after the dope had lost contact with the outer adapter. The undercut created a knife-edge that allows for the release of the PBO dope at the same time as the outer adapter. This modification worked well but poor film surface persisted.

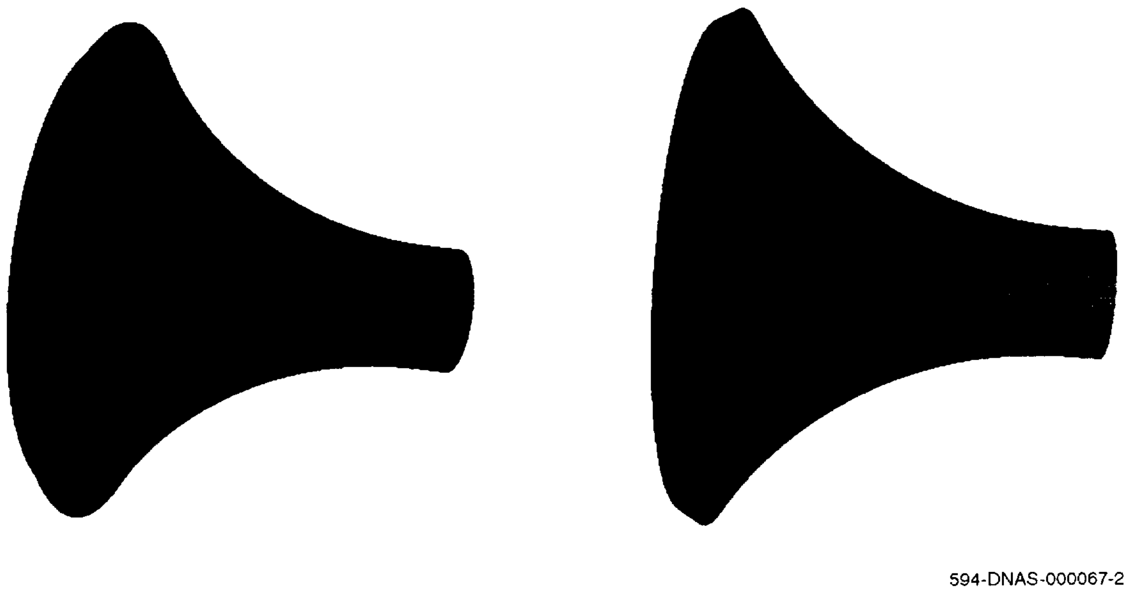

Figure 8. "Trumpet-style" die adapters

- Fabrication of an adapter set that created a 0.010 in. choke between in the inner and outer mandrel. The choke was designed to create a high shear zone to homogenize the dope and generate high axial draw on the dope as it was forced through the choke. The choke did not work as anticipated as flow through the die was not uniform (lack of backpressure). The rotating action of the die causes the PBO to be spirally forced out of the die without backpressure and complete die filling.

- "Choke" adapters were modified to increase the internal die to 0.090 in. The aim of this gap change was to increase the volume in the first compression section. This gap increase was still not large enough to produce a profile that had a continually decreasing volume and increasing velocity. The increasing volume results in the dope moving through the die in a "barber-pole" manner and circumferentially never fills the die.

- Fabrication of an adapter set whose geometry (shown in Figure 9) utilizes a discharge land that is parallel to the center-line of the die and has a decreasing cross-sectional area, thereby providing sufficient back pressure and increasing velocity to produce a uniform extrudate. With these new die adapters the radial increase in the die gap is achieved prior to the discharge end of the die. The discharge end has a 3.0 in. diameter, 2.0 in. long parallel land starting with a 0.051 in. gap and ending in a 0.040 in. gap.

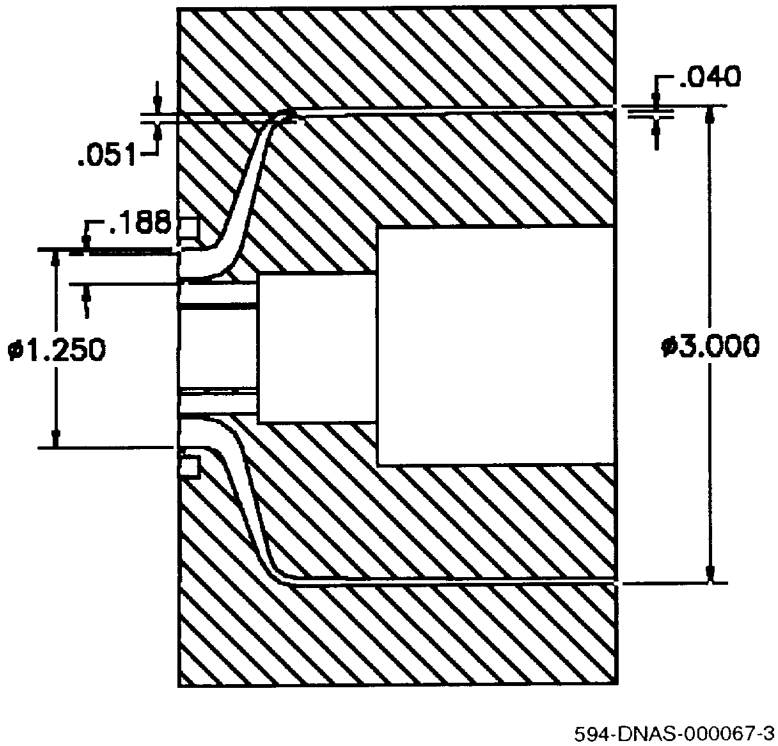

Figure 9. Standard die adapter geometry

3.2.2 New Extruder and Barrel

Scale-up to 7 in. diameter film required an output rate 2.3 times greater than that for 3 in. diameter PBO film extrusion. Foster-Miller's 3/4 in. Killion extruder with Hastalloy barrel and screw did not have the output capacity necessary to achieve this requirement. A new 1 in. extruder barrel and screw were fabricated from 17-4 pH stainless steel and Inconel respectively to provide a system with increased output capability. Both materials were shown to be resistant to the polyphosphoric acid in PBO. Various mixing technologies were investigated to incorporate the mixer into the screw. These mixing sections included:

- Left Hook Mixer (Scientific Process & Research, Inc.).
- CRD-4 Mixer (Rauwendaal Extrusion Engineering, Inc.).
- X-201 Mixer (Xaloy Inc.).
- Pulsar Mixer (Spirex Inc.).
- Maddocks (American Screw & Barrel Inc.).

After examining the above-mentioned mixer designs, the X-201 mixer was selected based on its dispersive mixing capabilities. A 24:1 L/D extruder screw (1.5:1 compression ratio) made from Inconel 625 with a X-183 hardfacing was fabricated with the X-201 mixer positioned at the end of the screw as shown in Figure 10.

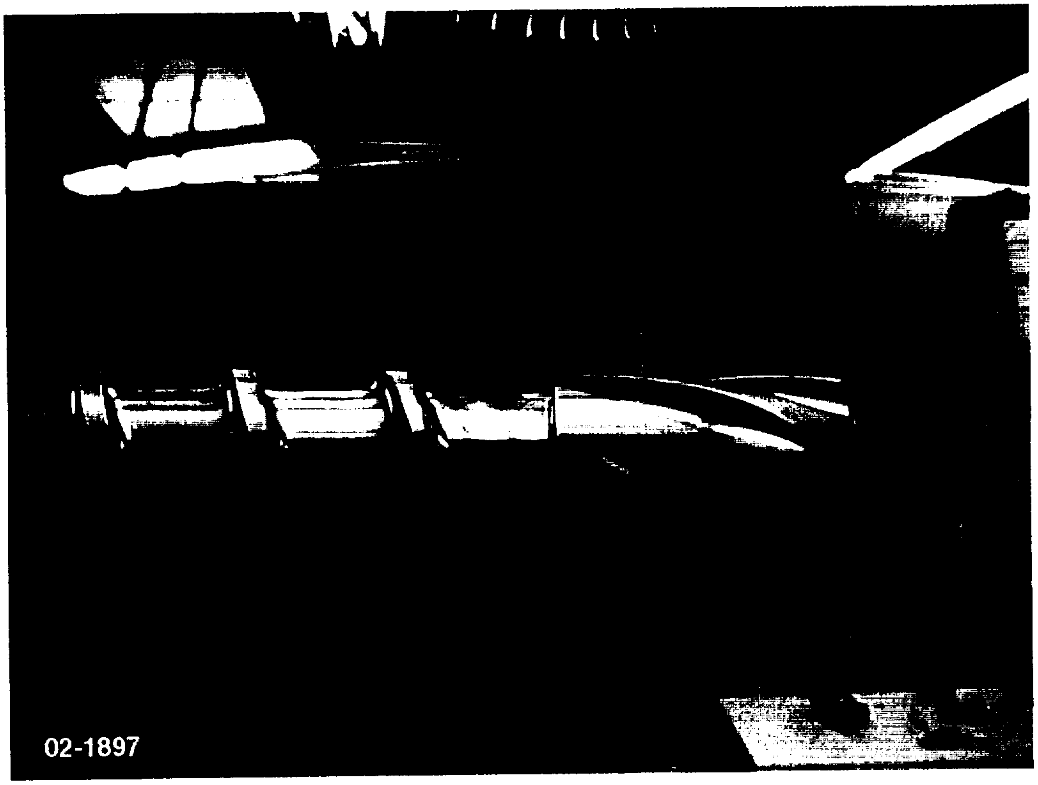

Figure 10. X-201 screw with mixer

3.2.3 Weeping (Sizing) Ring

The function of the sizing (weeping) ring is to control the bubble diameter and produce a uniform film. The ring for small diameter films was fabricated from porous stainless steel in a one-piece construction to the desired diameter and pore size. The sizing ring for a 3 in. bubble diameter was fabricated with a 2μ pore size. Thus high pressure can be generated between the steel ring and housing with minimal flow through the ring. A one-piece 7 in. ring could not be made from stainless steel (would have to be rolled and welded) and an alternative was sought. Ultrahigh molecular weight polyethylene (UHMWPE) was selected as a viable alternative. The pore size with UHMWPE could not be as easily controlled during the compression process or to the levels of the porous steel. Although the UHMWPE rings were not tested for pore size, the manufacturer, Pore Technology was able to effectively reduce the pore size from an estimated 35 to 40μ range down to about 5μ through several iterative processes. The key component to obtaining a low micron pore size was to start with a very fine particle size distribution in the base material. The larger pore size samples presented problems with excessive water flow through the ring.

Adjusting the water flow to decrease the flow rate caused the ring to not wet uniformly and the PBO film stuck at those "dry" spots. A high flow rate insures uniform "wetting" but excessive water dams up above the PBO bubble radius where it comes in contact with the ring. As water builds up it creates a little water dam where the PBO film coagulates before the film reaches the full diameter. The resulting effect, as shown in the right-hand sketch in Figure 11, is

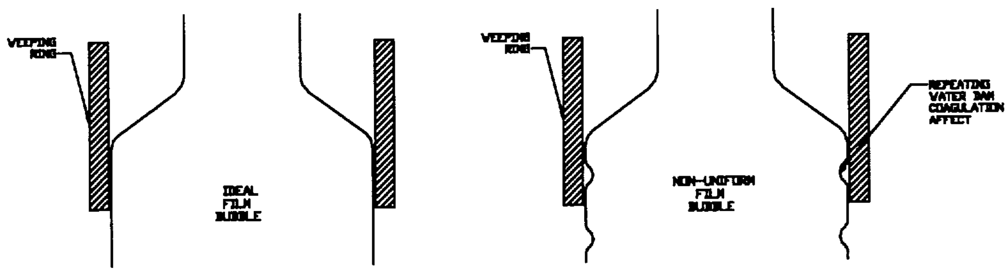

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Figure 11. Film bubble diameter profiles

a pattern that keeps repeating itself. The left-hand sketch shows the ideal process profile (the bubble is spaced from the porous ring surface for clarity. Ideally it is blown out against the ring). The size of the water dam then dictates the dimension at which the film will coagulate. Increasing the throughput rate helps to minimize the effect due to rapid haul-off and less water accumulation.

3.2.4 Implementing an Improved Take-Up System

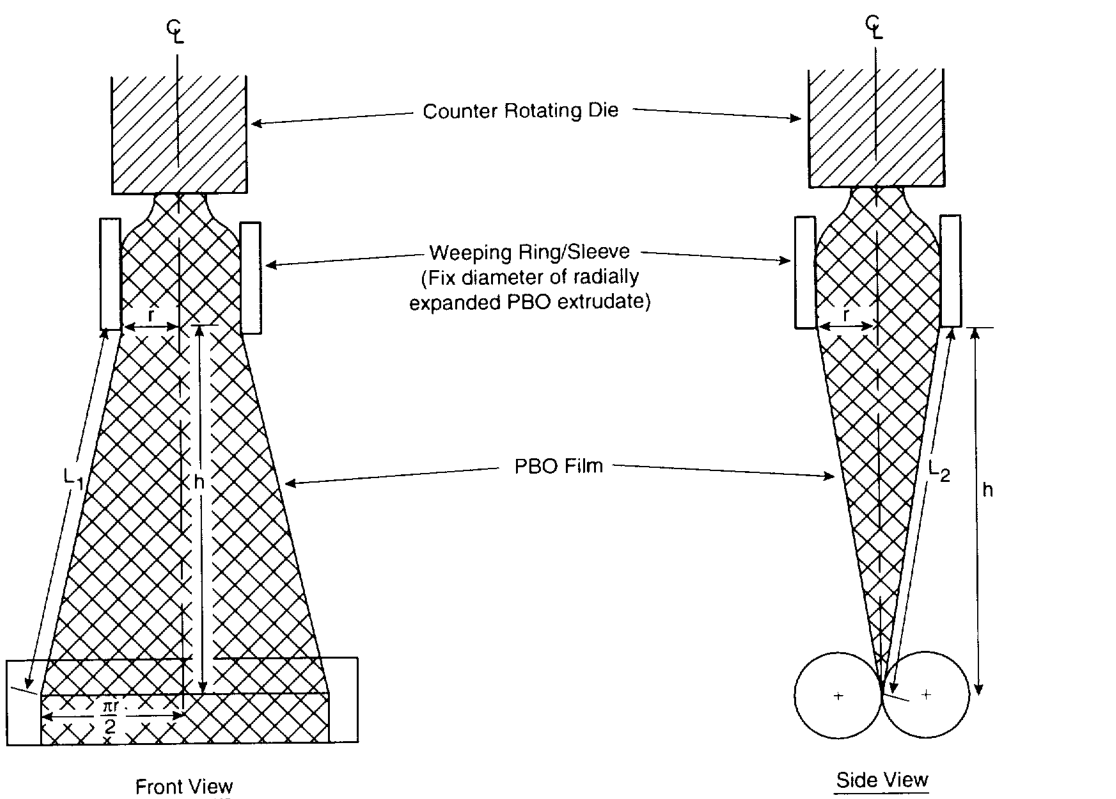
The take-up system plays an important role in the PBO extrusion process. Because PBO is extruded as an ultra thin film, the slightest fluctuation in take-up speed can significantly affect the gauge uniformity of the film (see Figure 6). The high modulus PBO film needs to be pinched correctly at the nip rolls to prevent wrinkling of the film as it is wound onto a submerged core. A larger, improved take-up system (VTA) was designed and fabricated to use in conjunction with the revised CRD. The new VTA was designed to incorporate four major improvements that were not possible with the smaller PBO take-up system (designed for 3 in. diameter bubble). These modifications include:

- Incorporating a large diameter idle roller that the film wraps around to seal off internal bubble water before being pulled upward toward the nip roll.
- A long collapsing zone.
- A sequential geometric transition where the film transitions from a circular profile (7 in. diameter) to a square profile (5.5 in. square) before collapsing to a flat ribbon (11 in. layflat).
- A precise clutch and drive system for the winding rolls to reduce mechanically induced fluctuations in take-up speed. Constant drawing of the extruded PBO film is critical for maintaining consistent gauge uniformity and diameter consistency.

3.2.5 Film Take-Up System Considerations

The two major features incorporated into the new PBO film take-up system to minimize film flaws generated by the collapsing process were introduction of a long collapsing zone and sequential geometric transition. The trigonometric relationship from collapsing a circular tubular product into a two-sided flat structure is illustrated in Figure 12. In this process, the length of the film from the point where it leaves the weeping ring/sleeve to its point of contact on the nip roll should be the same whether the process is viewed from the front or side. The length of the extruded film for both views is respectively labeled L_1 and L_2. Clearly L_1 and L_2 are not equal as shown by the respective formulas presented in Figure 12. In conventional blown film extrusion systems this difference in lengths (i.e., L_1 and L_2) is easily handled by the film take-up system since the film product has relatively low modulus and high elongation characteristics. PBO films, however, have very high modulus and very low elongation properties making it virtually impossible for the film to stretch to account for the difference in L_1 and L_2. As a result, PBO films when extruded tend to form wrinkles during the take-up process.

Two take-up system modifications were employed to help minimize these PBO film imperfections. These included increasing the length/height (h) between the end of the weeping



$$L_1 = \left[h^2 + \left(\frac{\pi r}{2} - r\right)^2\right]^{1/2}$$

$$L_1 = \left[h^2 + r^2\left(\frac{\pi^2}{4} - \pi + 1\right)\right]^{1/2}$$

$$L_2 = \left[h^2 + r^2\right]^{1/2}$$

Figure 12. Geometry of PBO film as it transitions from a circular to flat cross section

ring and the nip rolls, and providing a more gradual transition in geometry to reduce film stresses.

Increasing the Height of the Take-Up System

By increasing the height of the take-up system ("h," shown in Figure 12) the difference between L_1 and L_2 can be reduced. For example if h is set at 18 in. and r = 2 in., the difference between L_1 and L_2 is ≈0.07 in. If h is increased to 60 in. with r still equal to 2 in., the difference between L_1 and L_2 is reduced to 0.02 in. As a result of this analysis, the new CRD take-up system was designed to use the maximum ceiling height available in the Foster-Miller extrusion laboratory.

Geometrical Transition for Extruded PBO Film

Foster-Miller carefully analyzed the geometry of collapsing a tubular PBO film extrudate and its impact on creating film imperfections. This analysis indicated that by sequentially changing the tubular cross section of the film to one with a more-square cross section before the film moves to the nip rolls, the difference between L_1 and L_2 can be virtually eliminated. This is graphically demonstrated in Figure 13. In fact, if the extruded film can be geometrically altered to assume a perfect square cross then L_1 and L_2 would be equal as shown by the equations presented in Figure 13.

In order to increase the precision and consistency of the wind-up system, the PVC continuous belt was geared to the nip rolls at the top of the take-up assembly. By driving the belt at the same rate as the nip roll, less stress is placed on the PBO film as it overcomes friction against a stationary belt and moves through the two idle rollers. Constant drawing of the extruded PBO film is critical for maintaining consistent gauge uniformity and diameter consistency.

3.2.6 Results of VTA

The continuous PVC belt shown in Figure 14 was designed to help pull the PBO at a consistent rate to the windup and help support the PBO film during the extrusion. The large idle roller was completely submerged in a tank of water to complete coagulation and help seal the film bubble so that the water volume inside the bubble remained constant. The bubble was internally filled to the top of the V-shaped collapsing shed to ensure that the PBO did not collapse inward due to external water pressure. Consequently, the internal water generated excessive film pressure against the V-shed and PVC belt causing the belt to stall. The system was run without much difficulty but without the internal water. This resulted in the bubble collapsing inward and developing wrinkles due to the collapsed nature of the tube. Due to the technical difficulties associates with producing a 0.3 mil thick homogeneous PBO and the budget and time constraints of the program, we decided to terminate use of the VTA and return to the smaller take-up system. Though the smaller system had recognized problems (mostly with wrinkling during bubble collapse), we were comfortable that we would be able to produce films that, though not optimal, would meet the requirements of the program.

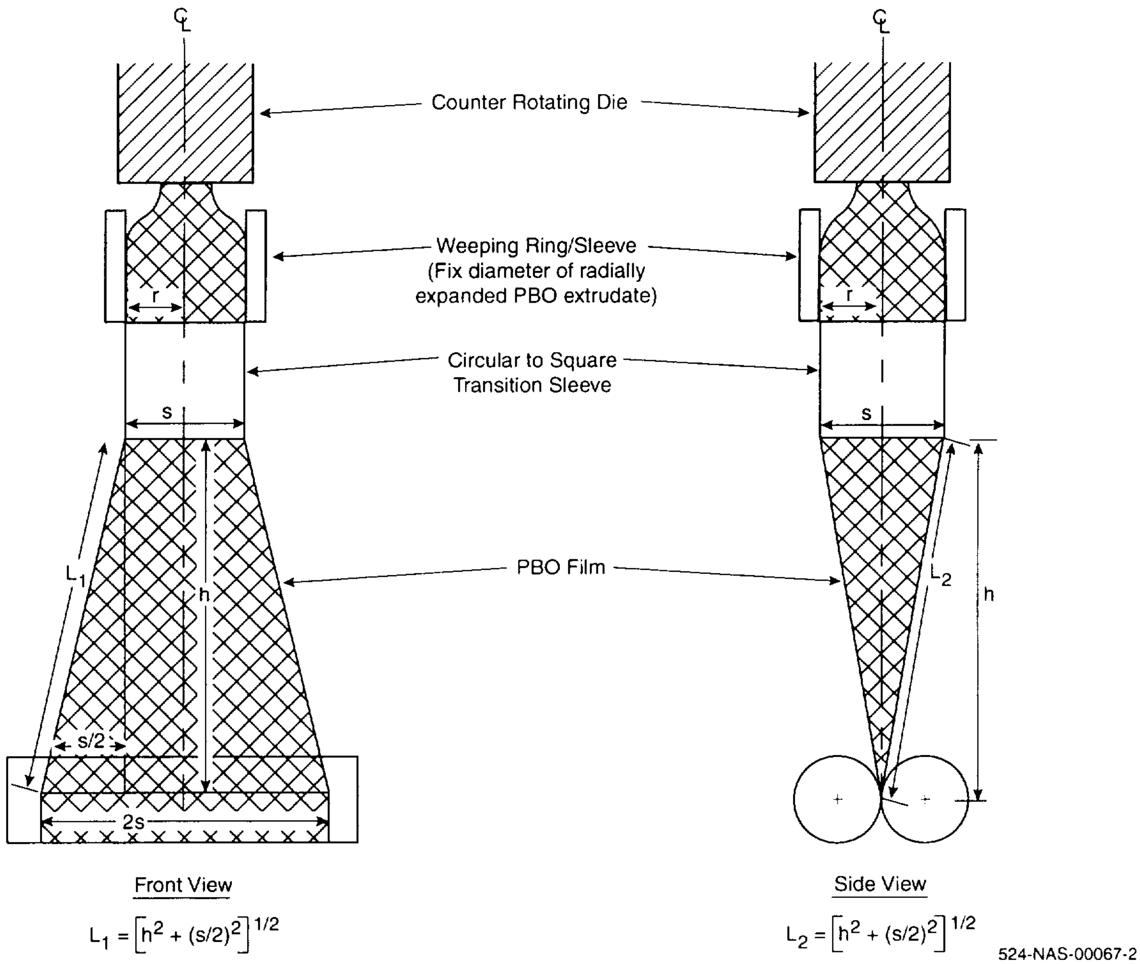


Figure 13. Geometry of PBO film as it transitions from a round, to square to flat cross section

3.3 Task 3 - Post Processing PBO Film

The PBO film produced in the previous task needs to be post processed to achieve its extraordinary mechanical and barrier properties. The post-extrusion processing involves a washing and heat treatment process to thoroughly dry out the film. The washing involves exchanging all of the polyphosphoric acid within the PBO film structure with water until the wet film exhibits a neutral pH value (5 to 7). Heat-treatment is performed under axial and hoop tension in a specially designed vertical convection oven purchased under a NASA-AMES contract during Venusian Balloon development. The PBO film, which is produced from a 14.6 percent solids solution, will shrink approximately seven times when the film is dried. Application of axial and hoop tension ensures that the reduction occurs through the thickness rather than the length or diameter. The thickness reduction ensures that the dried film is fully compacted and will attain maximum mechanical properties.

The oven was equipped with one pair of 7 in. mandrels for securing and drying a single 100 in. length of PBO film. A second pair of mandrels, shown in Figure 15, was installed

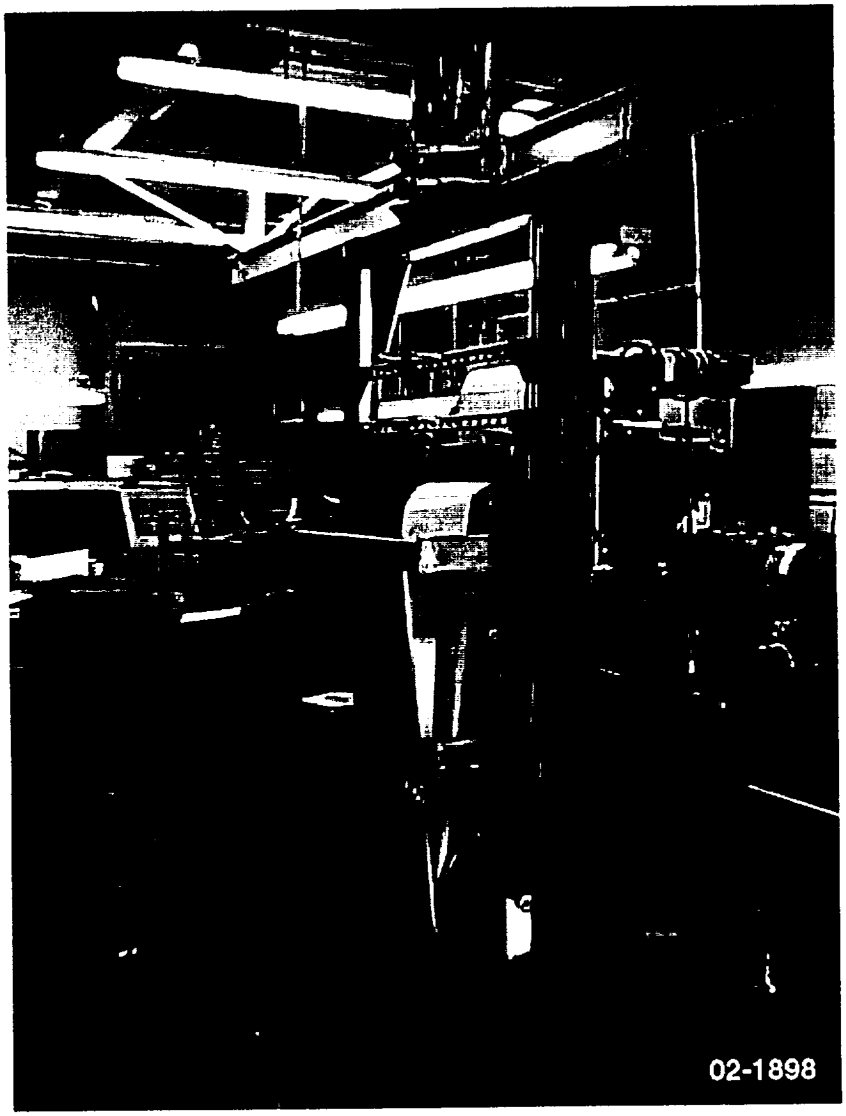


Figure 14. Vertical take-up assembly

adjacent to the original mandrels inside the oven. Each mandrel is equipped with individual regulators and gauges for monitoring and controlling axial and hoop stresses during the drying cycle. The standard PBO drying cycle, which took 19 hr plus cooling time, was modified to reduce the time. The standard cycle was difficult to complete within 24 hr, as the oven did not have active cooling to return the temperature to room temperature. The shorter cycle allowed the PBO film to dry during the day for 10.5 hr and then have enough time to cool overnight so that the oven was at room temperature the next day to dry another set of tubes. Tensile properties and oxygen permeability were measured on 3 in. diameter films which were dried in a ceramic tubular furnace utilizing the two drying cycles shown in Figure 16. The tubular furnace has more precise pressure control to apply axial and hoop stress to the PBO film but is limited to films of 4 in. diameter or less. The results indicated that there was no significant difference in properties (shown in Appendix A) with the shorter drying cycle thus it was established as the normal drying cycle for this program.

Figure 15. Two mandrel drying assembly

3.4 Task 4 - Construct and Test Prototype PBO Seams Joining Techniques

The balloon seams must exhibit all of the extraordinary mechanical and physical properties exhibited by Foster-Miller's biaxially-oriented PBO. Foster-Miller planned on modeling the Phase II seam design after the successful "lap-shear" type used during Phase I. However, Foster-Miller and Raven representatives agreed that it would be beneficial to produce the seam on commercially available equipment (ideally, Ravens' continuous sealing equipment). In addition, the adhesives (i.e., Master Bond's Supreme 10HT) investigated during the Phase I are either two-part or temperature cured epoxy systems. Although these epoxies meet the criteria for adhesion, permeability, and temperature stability they are not a viable option for the fabrication of a planetary aerobot. The epoxies are extremely brittle and stiff making it impossible to fold the balloon into the necessary packaging for launch. It was Raven's opinion that the pressure sensitive adhesive (PSA) that Raven uses to fabricate their polyolefin-based weather balloons will meet the requirements for this program. The PSA, Arclad 7876 (2 mil) and 8026 (1 mil) are silicone-based adhesives that offer excellent high and low temperature resistance.

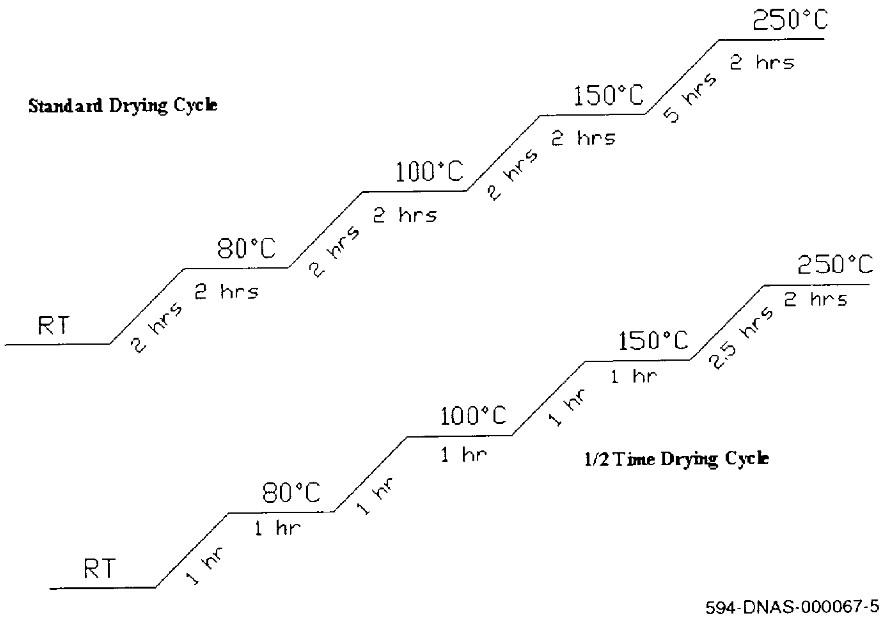


Figure 16. Timing cycles for drying PBO film

Raven used PBO samples (film thickness was slightly thicker than the film used to construct balloons) to produce prototype seams using the Arclad 7876 tape to form a 1-1/2 in. taped butt seam. The seam joint was constructed by "butting" the edges of two pieces of PBO film up against each other and then laying a strip of adhesive tape on each side of the seam. Another piece of thin PBO film was applied to the backside of the double-sided PSA to help maintain the high barrier properties and keep the balloon weight down. Seam strength as a function of tape width and adhesive thickness was tested for yield at 23°C, -80°C and -100°C. Differing widths of tape and corresponding seam strength were also evaluated to reduce the overall weight of the balloon. Figure 17 shows a typical seam configuration for a 1 in. x 1 in. seam (for clarity, the PBO film and PSA layers are not drawn to scale). The 1 in. x 1 in. configuration was chosen as a compromise between weight savings for a narrower seam and improved permeability with a wider seam.

3.4.1 Test and Analysis Results

Raven Industries fabricated and tested three different seam configurations using Foster-Miller's PBO film. (This film was left over from a previous program and was 0.010 to 0.013 mm (0.4 to 0.5 mil) thick.) Testing was performed at three different temperatures, 23°C, -80°C, and -100°C. On average, the tensile strength of the PBO remains comparatively constant from room temperature to -100°C. The seal comparison data indicates that the Arclad 7876 tape provided a quality seal and would not require any additional sewing to reinforce the seals. This test data indicates that the tensile properties of the PBO seams are very similar to the neat film

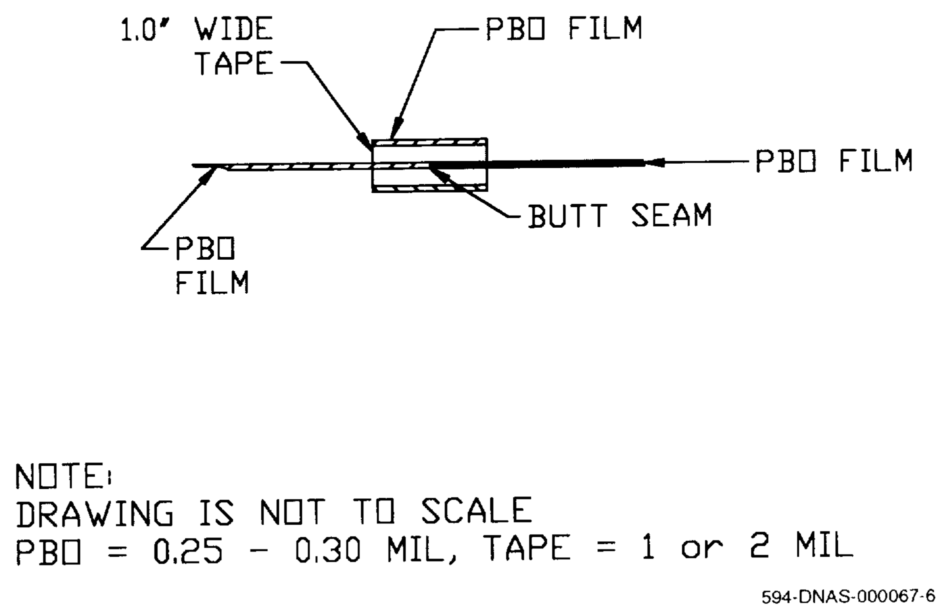


Figure 17. Typical PBO seam configuration

data where there is little change in tensile properties as the test temperature gets colder. Visual observation of the test specimen revealed that the film was failing before the PSA. This is a clear indication that the adhesive strength of the PSA is comparable or better than the film transverse direction tensile strength. These test results also indicate that the tape width can be minimized with minimal impact to the yield strength properties thus lowering the overall balloon weight. A summary of Raven butt seal data is shown in Table 5 (see Appendix B).

The effect of gage length on the ultimate tensile strength of the seal was also determined. The data in Figure 18 shows the effect of test gage length upon the UTS data of the seal. The 5 cm gage length is in accordance with the ASTM F 88 process to establish the true seal strength. The short gage length eliminates failure modes not associated with the seal's strength. In the cylinder pressurization tests, the failures occurred in the film away from the seal.

Table 5. Summary of Raven butt seal data

	Tensile Strength (MPa)		
Temperature	23°C	-80°C	-100°C
PBO Film (MD)	469 - 552	441- 524	427 – 448
PBO Film (TD)	386 - 427	441 - 469	469 – 503
1.5 x 1.5 seam	359 – 383	448 - 500	465 – 521
1.0 x 1.0 seam	377 - 427	359 - 403	431 – 483
1.0 x 0.5 seam	300 - 338	393 - 524	431 – 445

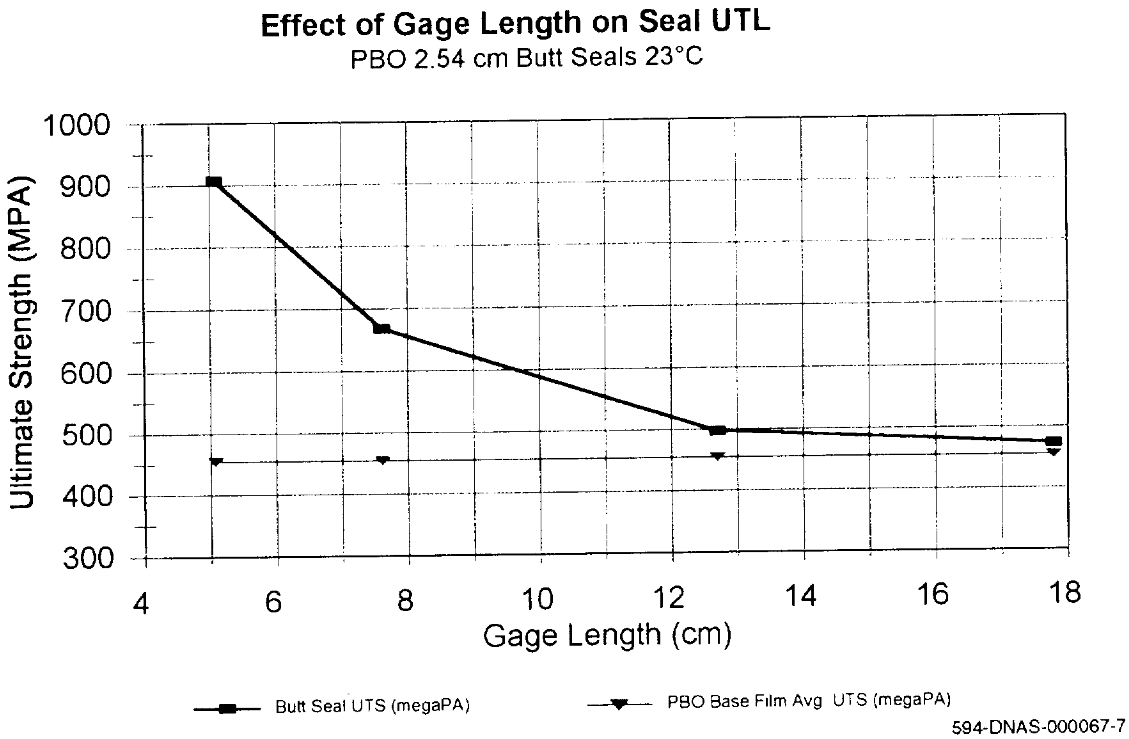


Figure 18. Effect of gage length on seal UTS

The sealing method also proved to be crucial in obtaining optimum bond strength of the seam. Application pressure and wetting of the PBO surface are critical to optimize the strength of the bond. The PBO /AR7876 adhesive tape when applied with the Raven sealer at 65°C or higher and 40 psi pressure produces seal strengths that are greater than the PBO film tensile strength at -100°C. However, small balloon diameters (like the 1m model balloons) cannot be fabricated with the Raven sealer and had to be ironed out with a hand patcher to improve the wetting. Hand patched 15.2 cm diameter cylinders had seal failures of approximately 335 MPa at -80°C (lower than anticipated). Seal strength measured on both hand and machine sealed seams at 23°C indicate that the machine-made seams resulted in seal strengths 16 percent higher than the hand sealed seams (1100 MPa compared to 950 MPa). (The results are shown graphically in Figure 19.) The sealing machine is able to more accurately apply heat and pressure at a constant rate compared to the hand operated process.

3.5 Task 5 - Test PBO Film

3.5.1 Gauge Uniformity

PBO film with uniform gauge is vital to produce lightweight balloon and still maintain all the necessary strength to cope with anticipated balloon stresses and exhibit high barrier properties. A three-dimensional thickness map was performed on a piece of film 22 in. wide x 18 in. long as shown in Figure 20 (thickness in mils). Thickness measurements were taken at approximately 1 in. spacing, both horizontally and vertically using a Fischer Permascope®, which uses magnetic

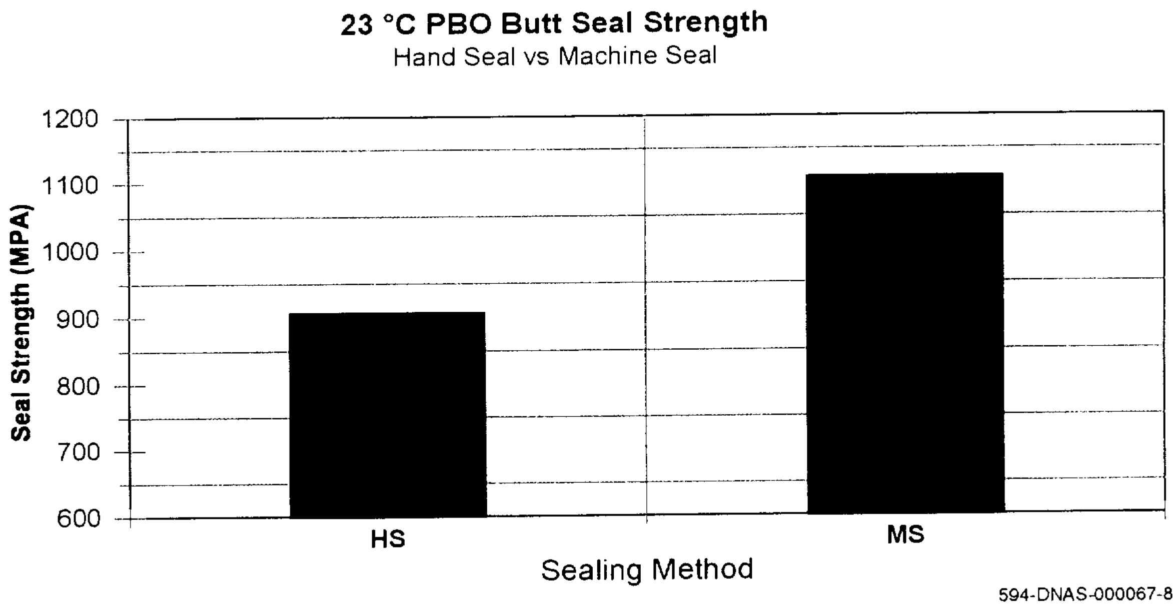


Figure 19. Effect of sealing method on seal UTS

induction to determine the spacing between the probe and an iron base. The results of the mapping indicate that the average thickness of the film is 0.271 mil (0.000271 in.) with a standard deviation of 0.053, which translates to a 19.5 percent deviation. This deviation is greater than anticipated. The cause for the deviation can be attributed to two different aspects of the extrusion; die mandrel concentricity (run-out) and PBO dope homogeneity. The major causes for the variation appear to be the clumps of the crystalline molecules (dark brown splotches) in the PBO dope that were not sheared out during extrusion (shown in Appendix A). The only way to produce a homogenous film with the available die configuration was to generate greater draw to stretch out the crystalline sites. Unfortunately, this resulted in a film that was ultra thin, less than 0.1 mil thick. Isolating the mechanically induced die variation from the PBO dope variation was impossible to determine. The die concentricity was measured after assembling the die and the runout measured ±0.001 in. on a 0.4 in. gap.

This equates to a 2.5 percent deviation that can be attributed to the die concentricity. A visual inspection of the film indicates that the film did not have repeating spiraling thin pattern that would be indicative of mandrel non-concentricity.

3.5.2 Tensile Properties (at 77°K and 295°K)

Tensile properties of PBO film were measured at 77°K and 295°K. The data as shown in Table 6 indicates that PBO retains most of its mechanical properties or is unaffected by sub-ambient temperatures. Although the data appears to decrease by 15 percent in the machine

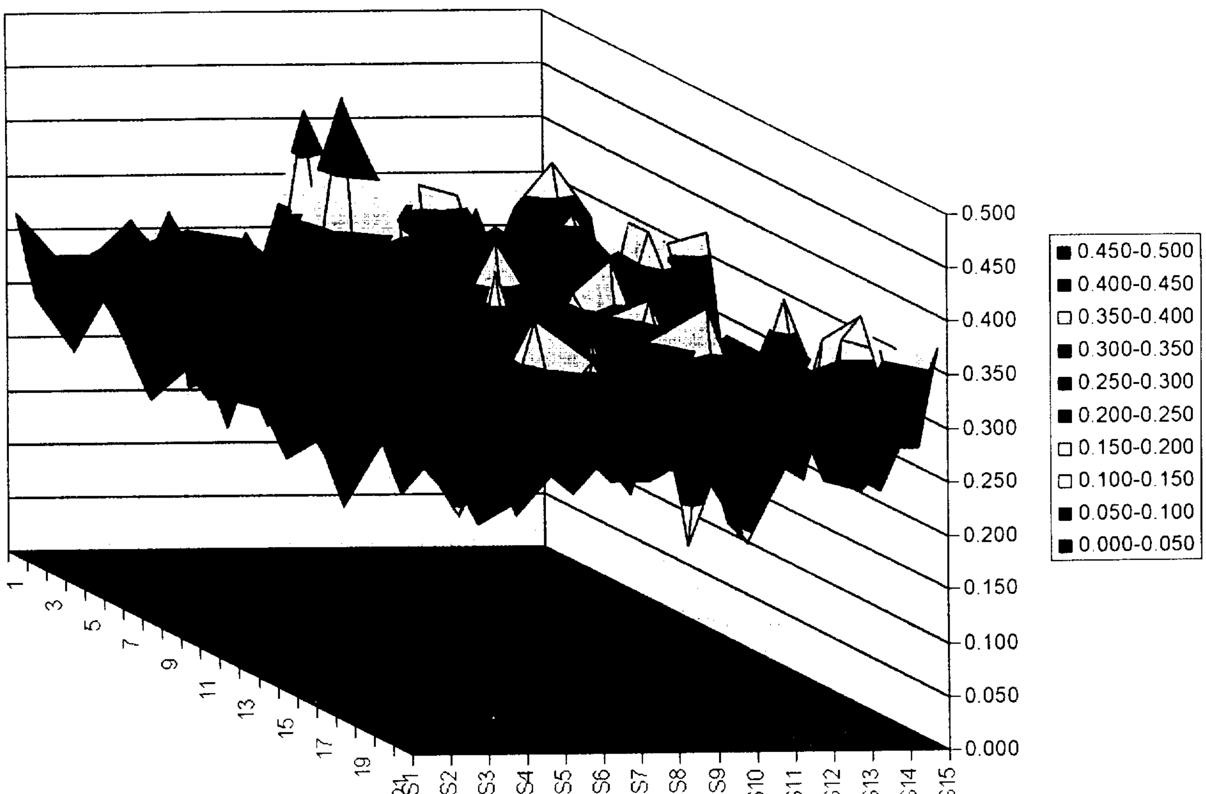


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Figure 20. PBO film thickness map

Table 6. Tensile properties at 77°K and 295°K

	MD	MD	TD	TD
Test Temperature	295°K	77°K	295°K	77°K
Tensile Strength (MPa)	1082.5	834.3	565.49	599.97
Tensile Modulus (GPa)	44.0	49.9	30.8	33.4
Strain at Break (%)	5.23	2.39	2.96	1.86
Average Thickness (mil)	0.27	0.27	0.27	0.27

direction (MD) as the temperature decreases, it increases by 19 percent in the transverse direction (TD). The decrease in the strength of the machine direction samples may be caused by the knurled grips. The cryogenic temperature testing requires a mechanical grip that will not freeze when submerged to approximately 77°K. A smooth grip surface leads to sample slippage while a knurled grip can cause the sample to tear and fail at the grip/film interface. A number of the machine direction tested samples broke at the grip thus the mechanical properties were impacted by induced stresses at the grip. The transverse samples all broke within the 3 in. gauge length and were not impacted to the grip. Since the MD strength (including grip breaks) was still higher than the TD (no grip breaks), the data was deemed satisfactory.

3.5.3 Oxygen and Hydrogen Transmission

Oxygen and hydrogen transmission rates were determined on both PBO film and seam sections. The testing was performed by MOCON unless otherwise noted. The results published in the draft final showed permeation rates higher than expected. MOCON had not tested for leakage through the seals and had great difficulty sealing the PBO films in the test chamber during the retest. The test procedure involves determining a leak rate to establish a true zero by subtracting out any oxygen that leaks through the seals. The process involves applying a nitrogen/hydrogen gas to both sides of the film in the test chamber. Thus any permeation attained can only be attributed to atmospheric oxygen leaking into the system and being detected by the oxygen sensor. MOCON determined the leak rates to be 0.094 and 0.057 cc/m^2 -day for the two tested samples. After testing with oxygen, the leak rates are subtracted from the oxygen transmission rate yielding a true permeation rate as shown in Table 7. Normalized for thickness, these values are extremely low (almost an order of magnitude lower than expected). Conversely, if the leak rates and permeation rates were combined the normalized results would be 0.002 and 0.001 cc-mil/100 in.^{2}-atm-day respectively which is still within the expected PBO permeability range. This indicates that the film tested was an extremely good barrier film. The seam samples developed by Raven Industries were at least one order of magnitude higher in permeability. MOCON was not able to seal the standard seamed sample against atmospheric oxygen. The seam (shown in Figure 17) has a thickness of 4.6 mil while the surrounding film (3.5 in. diameter) was approximately 0.3 mil thick. This thickness variation created a spot where the O-ring could not conform to provide the necessary seal. A modified test sample was produced where a 3 in. slit was cut into the 3.5 in. diameter test sample. The slit was then covered with the adhesive and PBO as in the fabrication of the continuous seams. This allowed for testing of a 3 in. long seam while maintaining a uniform one-layer thickness at the seal diameter. The results indicate that the seam is approximately one order of magnitude more permeable than the PBO film but still two orders of magnitude less permeable than Mylar. Hydrogen was not retested and no correlation can be derived based on oxygen data.

3.5.4 Scanning Electron Microscopy

The effect of imparting a fold on the PBO film surface was examined with scanning electron microscopy (SEM). One fold was made and the crease pressed flat by running ones fingers

Table 7. Permeability of PBO film*

Sample	Gauge	Gas Type	Transmission Rate (cc/m^2-day)	Permeability (cc-mil/100 in.^{2}-atm-day)
PBO Film (030602-1)	0.33	Oxygen	0.018	0.0002
PBO Film (030602-1)	0.29	Oxygen	0.008	0.0004
PBO Film (030602-1)	0.28	Hydrogen	41	0.76
PBO Film (030602-1)	0.29	Hydrogen	168	3.21
PBO Seam		Oxygen	2.03	0.04
PBO Seam		Oxygen	1.07	0.02
PBO Film (012999-1)**	0.25	Oxygen	0.3	0.003 to 0.005
PBO Film (012999-1)**	0.25	Oxygen	0.2	0.004 to 0.005

*Films being retested by MOCON to verify sealing efficiency.
**Tested at Foster-Miller using a MOCON 2/20 SM permeability cell.

along the length of the fold. This would at worst case replicate the folding required to package the balloon before flight. SEM examination was then performed on a control section (no fold) and the internal and external sides of the fold. Ten SEM microphotographs are shown in Appendix D. The analysis revealed, most importantly, that there were no cracks or pinholes created by the folding. However some fibril damage may have occurred. The ± fibril orientation reinforces the film and prevents the fold from propagating through the entire thickness. Figure 21 shows the internal side of the fold. The film has creased and acquired a slight cavity though no through thickness defect is evident. The photograph on the right reveals an "X"-like pattern that may be a result of another fold that was generated during the extrusion stage of the process. It appears as if the high modulus oriented fibrils are displaced through the thickness but does not generate tears or holes through the thickness.

3.6 Task 6 - Demonstrate Martian Environmental Compatibility

The ability for the balloon envelope to survive the Martian atmosphere is crucial, since the aerobot mission is anticipated to last approximately 100 days. A coating on the PBO film is the most likely solution to environmental compatibility issues, specifically UV radiation resistance and possible electrostatic buildup. Consideration must to placed upon the following characteristics:

- UV absorbing/reflecting ability.
- Flexibility.
- Coating/Polymer interfacial adhesion.
- Effect of coating process on PBO properties.
- Electrical Conductivity (if desired).

Foster-Miller has successfully coated PBO films with up to 1200Å of gold using a physical vapor deposition process coupled with a 50 to 100Å titanium tie layer and heat/radiation based

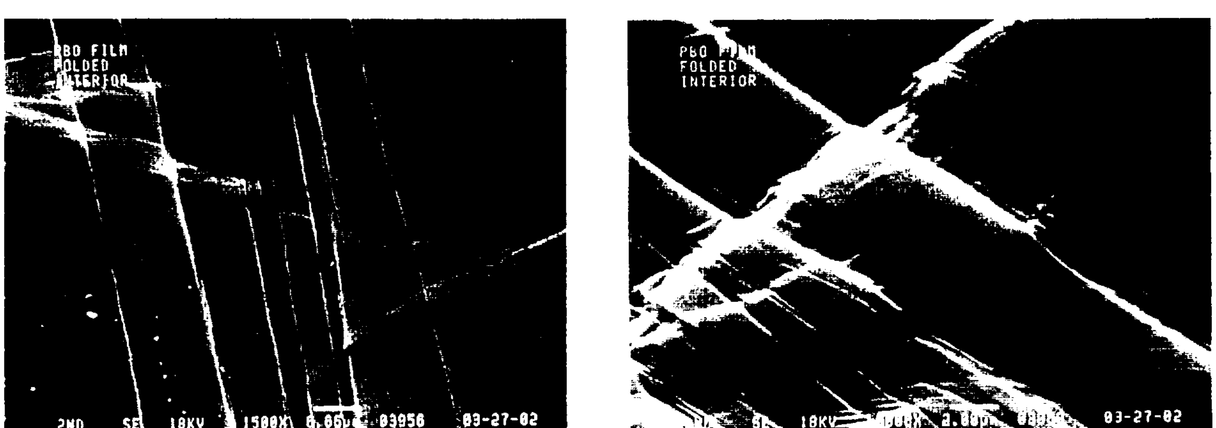

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Figure 21. SEM showing effect of ±orientation on a fold

surface pretreatment. This process is which is proprietary to Sheldahl Inc., has been proven to be successful in previous PBO programs and was not considered during this program. Two other coatings, silicon oxide (SiOx) and fluorocarbon were selected and deposited onto PBO films by MetroLine Industries (Corona, CA). Metroline's coatings are applied by Plasma Enhanced Chemical Vapor Deposition (PECVD) in a vacuum chamber at or near room temperature. Coating thicknesses can be varied from 50 to 3000Å. Two sets of fluorocarbon-coated samples were prepared. The first set has a coating thickness of ~770Å (77 nm) and the second set has a coating of ~1660Å (166 nm). Both fluorocarbon coatings are approximately 30 percent PTFE. Six silicon dioxide (SiOx) coated samples were also prepared and coated at thicknesses of 160 nm, 200 nm, 360 nm, 580 nm, 1000 nm and 1200 nm.

3.6.1 Strength Retention after UV Exposure

Raven Industries tested the previously mentioned coated film samples and an uncoated control after exposing the films to 340 nm UVA radiation at 45°C. Only three SiOx coated films (160 nm, 580 nm and 1200 nm) were tested in this matrix in order to keep the matrix from getting too large. The films were exposed for 725 hr (32.3 days) and mechanical properties measured before exposure (0 days) and after 10 and 32 days of exposure. The effect of UV exposure on the PBO film was measured as a percent retention of ultimate tensile strength.

Surprisingly, the data indicates that the thinner coatings provide better UV resistance for both coated materials and appear to provide adequate protection to UV radiation. In both material testing, the 160 nm coatings resulted in 84 to 86 percent retention of ultimate tensile strength. The control (no coating) retained 81 percent of its strength after 32 days. Although some of the data reveals a low absolute tensile strength, the differential before and after UV exposure is the real determining factor to UV resistance. Different thickness films were used due to the technical difficulties encountered during this program in producing good quality film. Material left over from the Phase I program was used for some of the coating evaluations. Retention of ultimate tensile is shown in Table 8 and detailed data appears in Figure 22.

Table 8. Retention of ultimate tensile strength

	Thickness mm	Ultimate Strength MPa	Ultimate Strength MPa	Ultimate Strength MPa	% UTS Retained 10 Days	% UTS Retention 32 Days
Days Exposed		0	10	32		
SiOx 1600	0.005306	1717.49	1862.77	1470.05	108.46	85.59
SiOx 5800	0.004793	1420.30	961.94	778.47	67.73	54.81
SiOx12000	0.011297	999.19	519.19	498.49	51.96	49.89
Fluorocarbon 770	0.011297	397.29	538.94	365.18	135.66	91.92
Fluorocarbon 1660	0.016090	340.77	318.99	285.86	93.61	83.89
Control - No Coating	0.014378	389.87	308.42	315.75	79.11	80.99

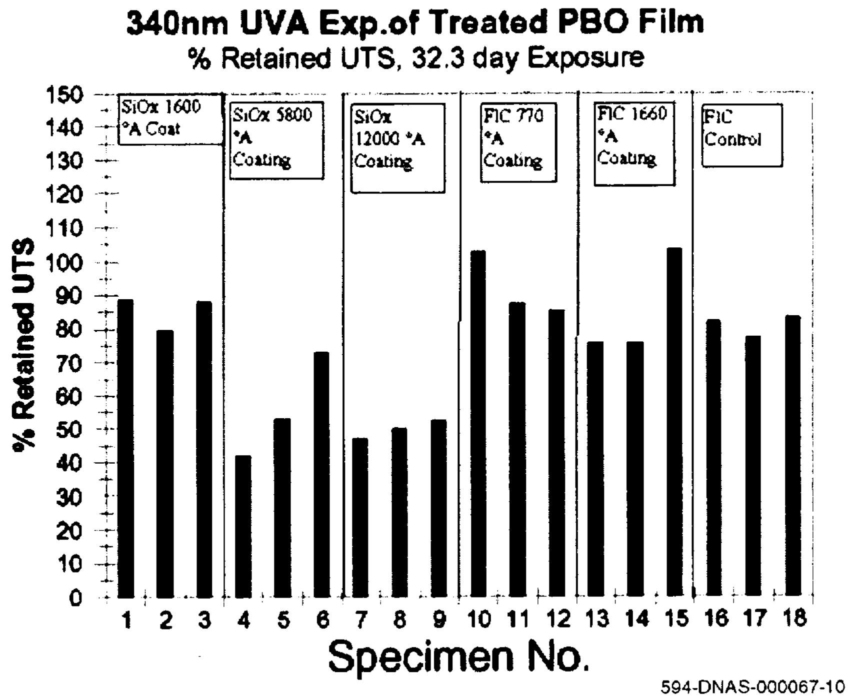


Figure 22. Individual retention of ultimate tensile strength

3.6.2 Optical Data

Raven Industries performed testing for optical data to aid with the balloon design. PBO films as well as taped seams were tested for transmittance, reflectance and emissivity. Transmittance and reflectance data are shown in Appendix E. When compared to Astrofilm, which is commonly used to make scientific research balloons, the PBO transmittance is lower (approximately half of the Astrofilm value) and the reflectance is greater (about three times as high). A possible cause for these higher reflectance values is the dark non-homogeneous "splotchy" marks on the PBO film. The dark regions, in addition to being thicker, also absorb more radiant energy thus lowering the transmittance value. According to Raven Industries, the fact that the transmittance and reflectance are higher than those measured for Astrofilm is not critical. The more important measure is that ratio of absorptivity to emissivity remains constant. A detailed summary of this data is shown in Appendix E.

3.7 Task 7 - Martian Balloon Prototyping

An engineering report will be provided by Raven Industries detailing the protocols established for the Martian balloon prototyping.

3.7.1 Cylinder Fabrication

Adhesive Research 7876 adhesive was applied to the 0.0038 mm (0.15 mil) film and 2.54 cm wide tape strips were sectioned from the prepared film. The material for the fabrication of two cylinders was sectioned from the PBO film so that the circumferential loading would be in the film's transverse direction. A minimal film thickness of 0.0038 mm was determined.

The cylinder seal for the first cylinder was prepared by aligning the film butt edges and applying the 2.54 cm tape by hand to both sides of the butt joint. The seal was then ironed with a 320°F hand sealing tool. The seal of the second cylinder was prepared by hand taping and then the taped cylinder was processed through the Raven sealer operating at 40 psi and 150°F.

The cylinder length was trimmed to yield a terminated cylinder approximately 50 cm. The cylinder was terminated on aluminum spools with ports for inflation and pressure monitoring.

3.7.2 Cylinder Testing Procedure

For testing, the cylinders were mounted in the Raven temperature test chamber with pressurization and monitoring tubes attached. The test chamber temperature was adjusted to -80°C and -100°C and then pressurization of the cylinders with helium began. The cylinder pressure was monitored with a pressure gage and a load cell. Pressurization in this closed chamber was limited to 4.5 psi.

Cylinder pressurization at 23°C was accomplished with the test chamber door open. Pressurization continued to cylinder failure. Butt seal tensile test specimens were sectioned from the ends trimmed of the cylinders and tested tensile strength at 23°C.

Two 1m diameter (shown in Appendix F) and two 1.5m diameter spherical balloons were fabricated and tested by Raven Industries. The two 1.5m balloons are being delivered to NASA-JPL for evaluation.

3.7.3 Balloon Fabrication

The balloon fabrication techniques and protocols used by Raven Industries are listed below:

Materials:

- *Gore material:* 0.0002 to 0.0003 in. PBO film.
- *Tape:* PBO film with Arclad 0.001 thick 8026 Adhesive.
- *Balloon end fitting assemblies:* Raven Dwg. 308670.
- *Gore pattern:* 308670 for 1m balloon and 308671 for 1.5m balloon.
- *End fitting sealant:* Schnee-Morehead SM5144 silicone sealant.

Fabrication Processes:

Tape Manufacture:

1. Apply the Arclad 8026 transfer adhesive to the selected PBO film using hand pressure.

2. Slit the adhesive coated film into 1 in. wide strips.

3. Process the strips through the Raven Hot Wheel Sealer operating at 150 to 180°F and 48 to 50 psi.

Gore Pattern Fabrication:

1. Select and inspect the Foster-Miller supplied PBO tubes for mechanical imperfections.

2. The selected PBO tubes for gore fabrication are oriented and positioned to minimize the wrinkles and maximize the dimensional accuracy.

3. The required gore pattern template is positioned and anchored in the desired location.

4. The gores are then sectioned from the film using a new razor blade. Extreme care is exercised to insure that the cut is uniform and there are no nicks, tears or other irregularities that would create mechanical weaknesses in the film.

5. The pattern is inspected and submitted for balloon fabrication when conformance is established.

Fabrication Methods for Taped Butt-Seal Constructed Balloons:

1. Seals for balloons larger than 2m and larger in diameter would be fabricated using the Raven Hot Wheel Sealer. Balloons with smaller diameter are fabricated using hand-sealing processes.

2. Each seal is made by positioning the gore edges to eliminate a gap and overlap. The 1 in. wide previously prepared tape is applied so that the butted gores line is in the middle of the tape as it is applied. The tape is firmly pressed by hand after application.

3. Prior to the closing seal, the 1 in. wide tape is applied to the opposite side of the initial taped seal. These seals taped on both sides are now carefully ironed by hand using a shoe iron operating at 300°F.

4. The finished seals are inspected for non-conformance.

5. The closing seal is now made using the above materials and processes. The closing seal is inspected for compliance.

End Fitting Application:

1. The sealed balloon carcass ends are laid out and the base and apex fitting location is determined and marked.

2. The fitting locations are reinforced for fitting installation with Raven SS10 tape.
3. The access termination holes for the fitting screws and access are trimmed into the reinforced area.
4. A 1/16 to 1/8 in. bead of SM5144 silicone sealant is applied to the apex and base fittings in the areas necessary to block the inflation gas escape routes.
5. The seal and prepared fittings are located in the designated areas and the closing hardware installed.
6. The hardware is secured to insure the designed performance of the balloon.
7. The balloon is then inflated and inspected for any non-conformance.

Balloon Pressure Test:

One of the model balloons was pressure tested by Raven Industries to determine maximum internal pressure capability of the balloon. Figure 23 shows the balloon inflated to 0.75 psi. The balloon went to a pressure of 0.92 psi before bursting (graphically shown in Figure 24). The film thickness in the area that burst occurred was only 0.12 mil corresponding in a stress of 72 ksi in the film at that point. The extremely thin section of film was unfortunate, as a more uniform

Figure 23. PBO balloon pressurized to 0.75 psi

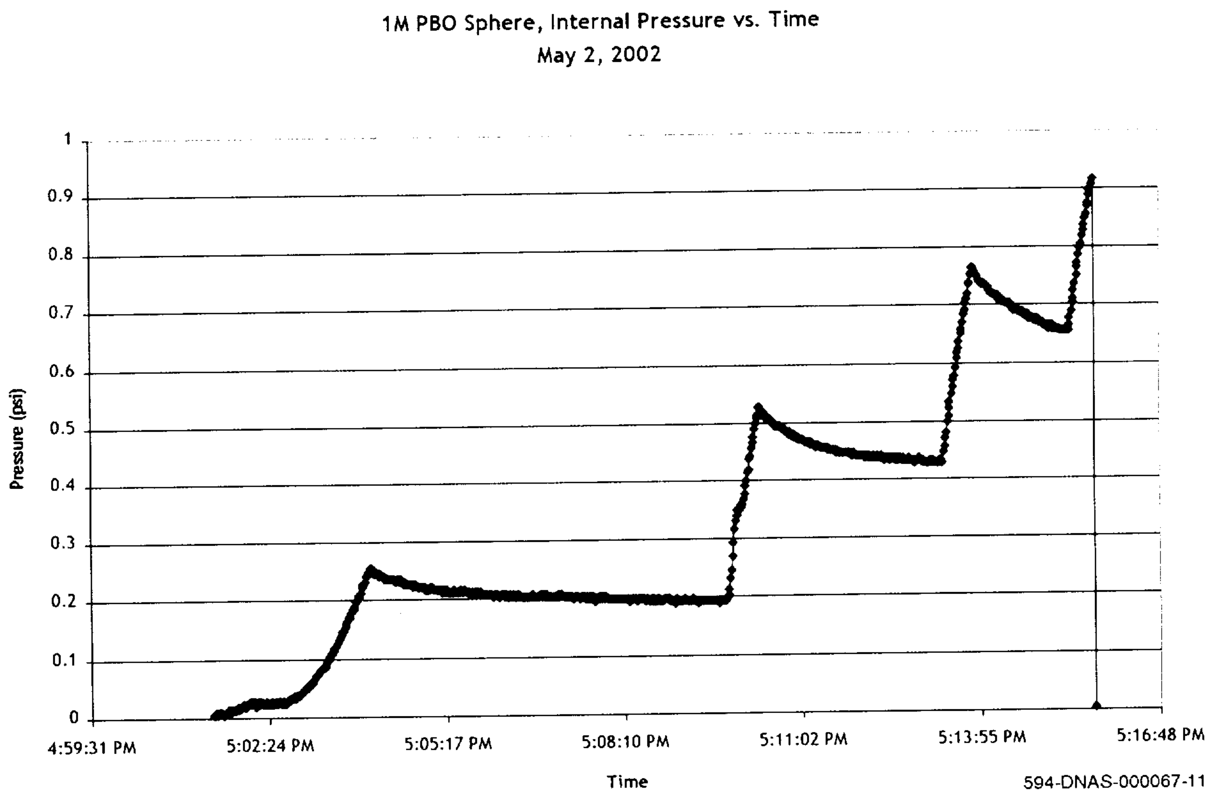


Figure 24. Pressure-time graph of burst test

(thicker) film thickness may have produced a greater bursting stress. The most consistent film was reserved for the two flight balloons that were designated as deliverables on this program. Films with greater gauge variation were used in the fabrication of the model balloons. This coincided with the success of the extrusion trials. The earlier trials yielded poorer film quality and these were the first films that were post processed and shipped to Raven for fabrication of the model balloons. The films sent for fabrication of the flight balloons, though still exhibiting greater than 10 percent gauge variation did not possess the ultra thin sections that were present in some of the earlier films. In retrospect, a flight balloon should have been burst tested to get a more representative bursting stress of the material properties.

4. CONCLUSIONS AND RECOMMENDATIONS

During this Phase II program, Foster-Miller demonstrated that biaxially–oriented PBO films can be scaled-up to meet the demands for an extended mission and variable altitude Martian aerobot envelope material. Although it would be desirable to scale-up the width of PBO film produced during Phase II by a factor of at least 3, Raven feels that full-scale Martian aerobot balloons –10m diameter or larger-could be fabricated from the present 22 in. width film. While this would involve significant additional seaming expense, the excellent qualities of the PBO film for Martian environments may well justify the increased cost.

APPENDIX A

Table A-1. Effect of drying time on mechanical properties and OTR

PBO Film	Drying Cycle		Tensile (ksi)	Modulus (Msi)	Strain at Break	OTR (cc-mil/100in.^{2}-atm-day)
012999-1	Standard	MD	107.42	6.22	3.03	0.021/0.003
012999-1	Standard	TD	59.26	3.30	2.49	0.005/0.002
012999-1	1/2 Cycle	MD	121.79	6.70	4.25	0.005/0.005
012999-1	1/2 Cycle	TD	50.02	3.71	1.90	0.004/0.002

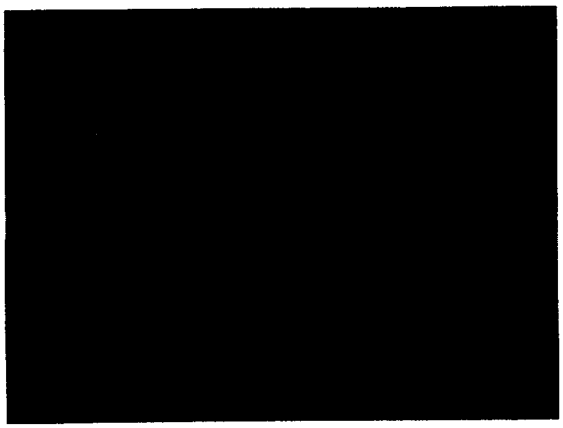


Figure A-1. Non-homogeneous 0.3 mil film

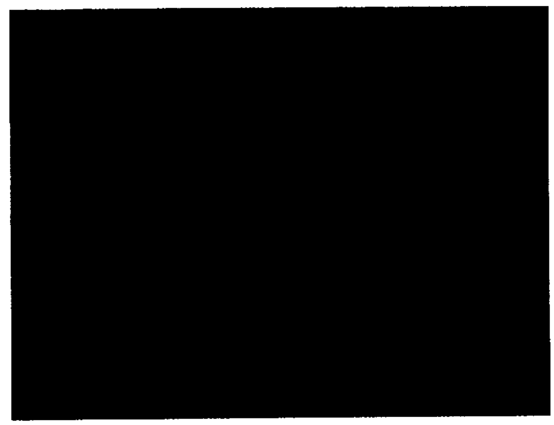


Figure A-2. Non-homogeneous 0.3 mil film

Figure A-3. Homogeneous 0.2 mil film

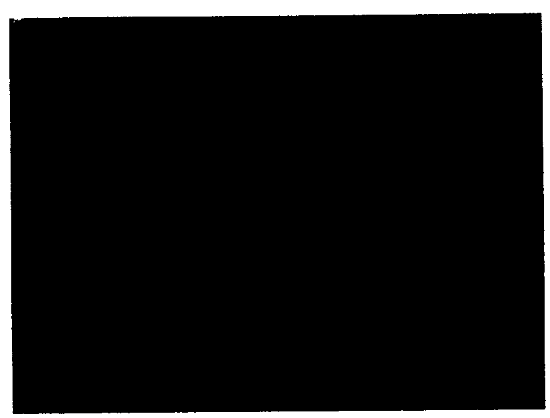


Figure A-4. Homogeneous 0.2 mil film

APPENDIX B

SEAM DEVELOPMENT DATA

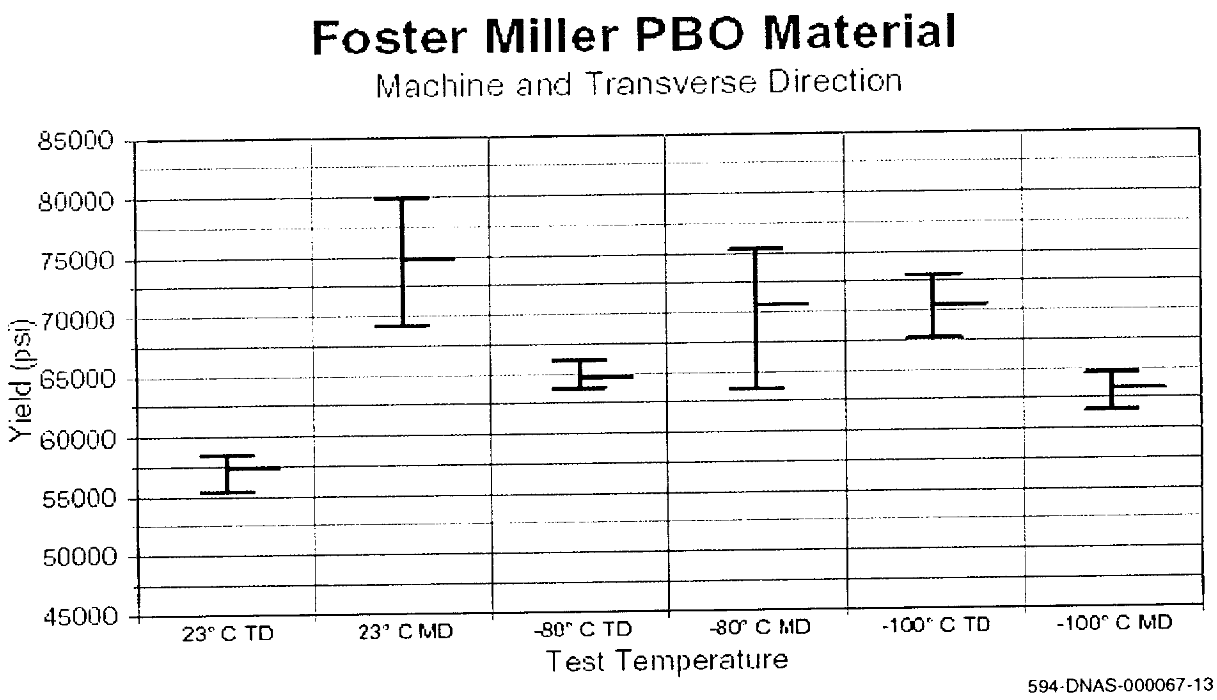


Figure B-1. PBO tensile strength

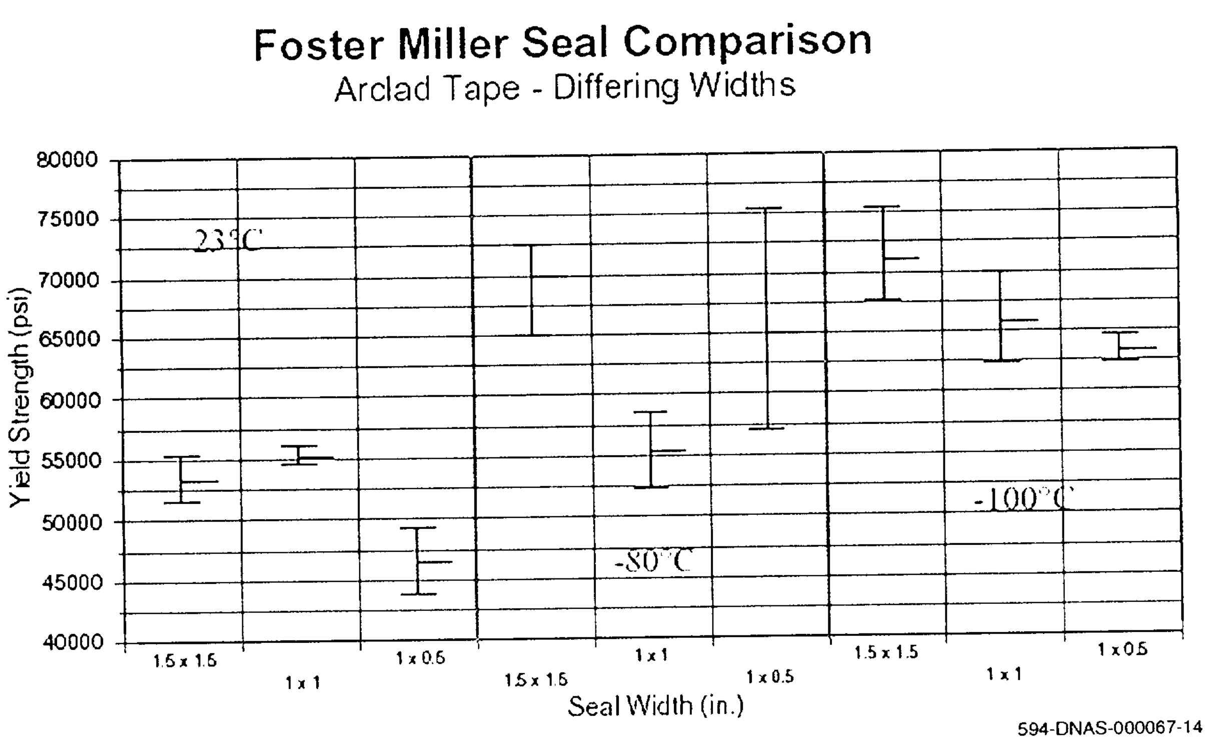


Figure B-2. Seal tensile properties versus different tape width combinations

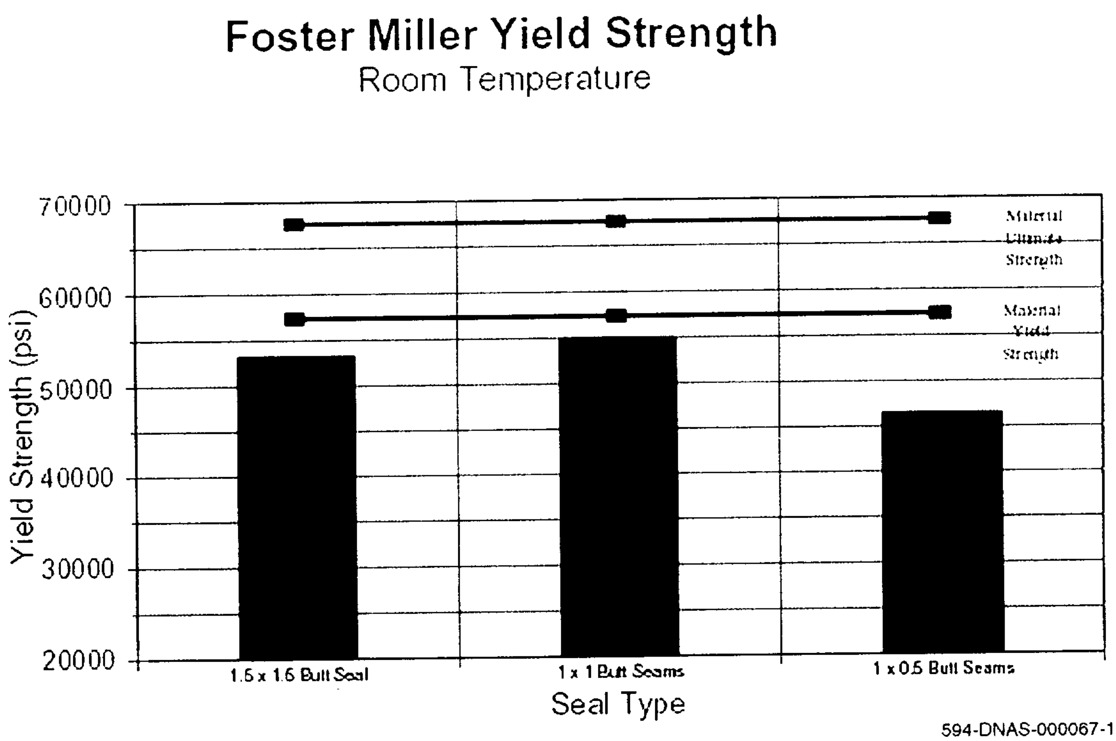


Figure B-3. Effect of seam tape width on yield strength at 23 °C

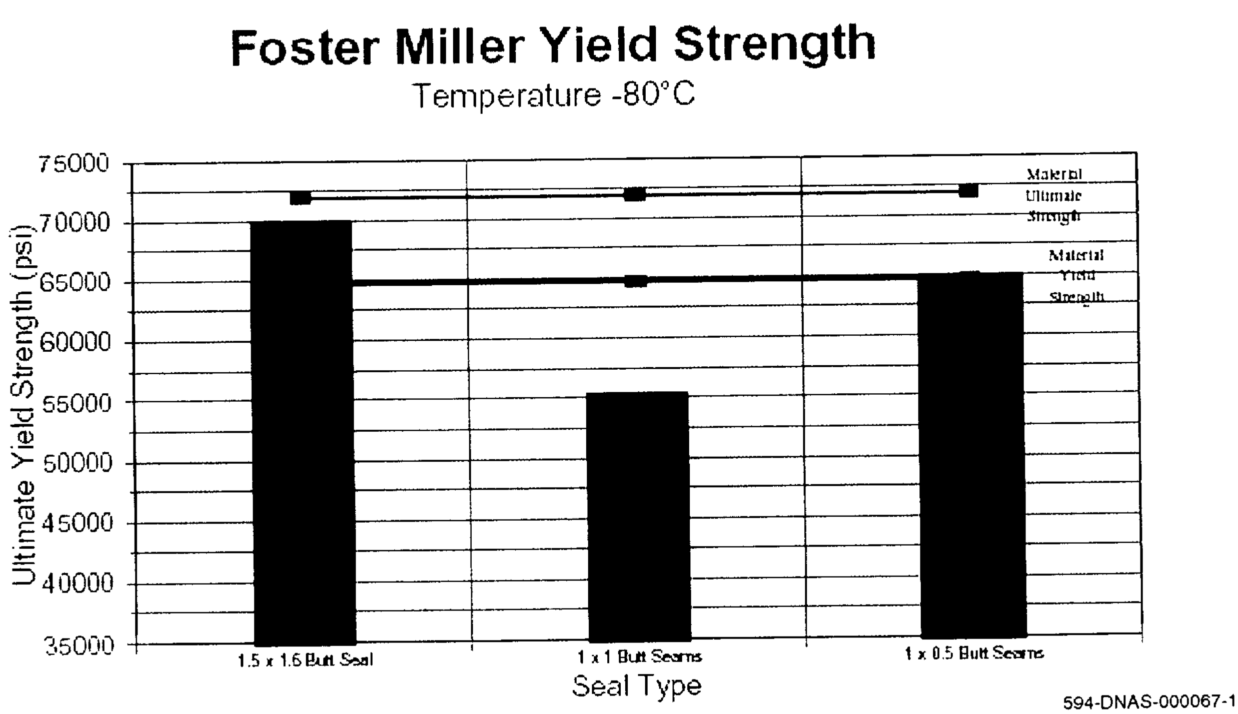


Figure B-4. Effect of seam tape width on yield strength at –80 °C

APPENDIX C

MARTIAN COMPATIBILITY DATA

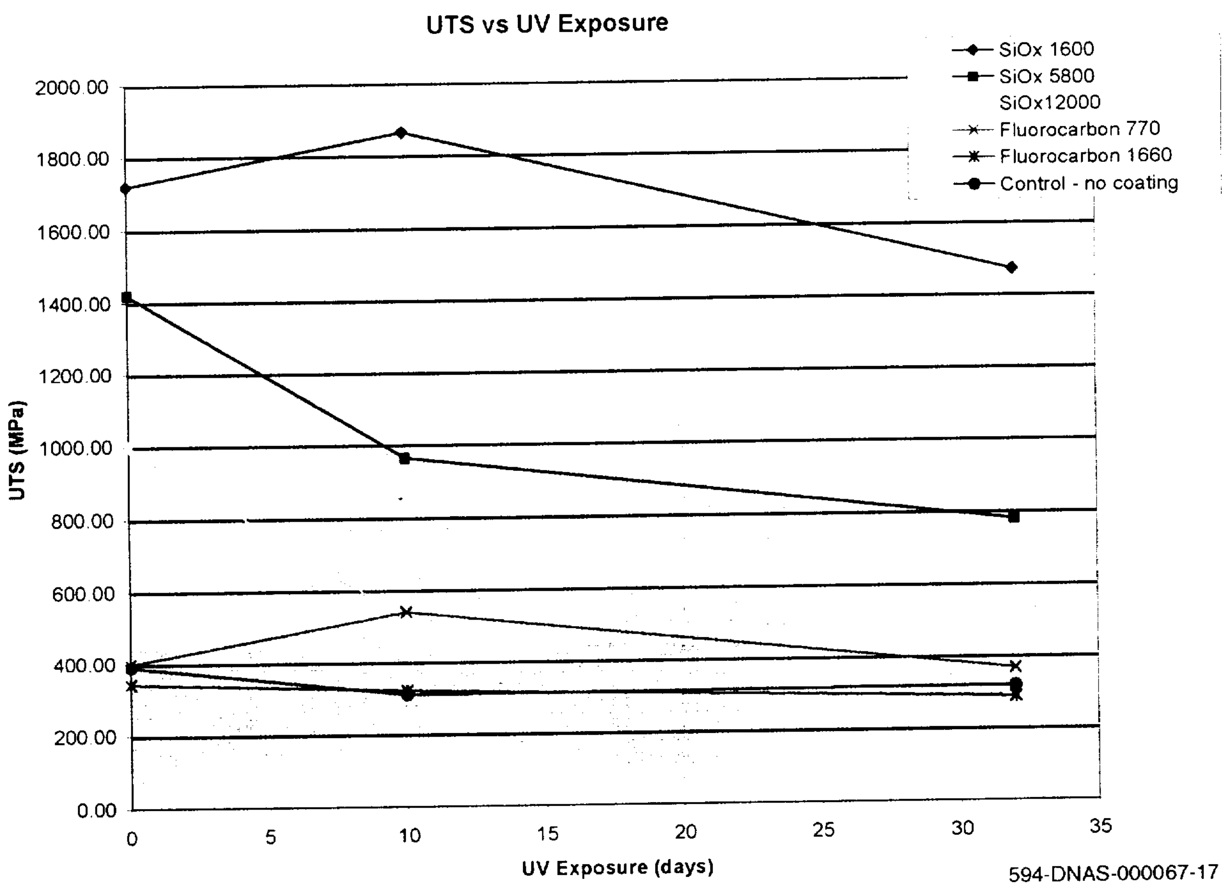
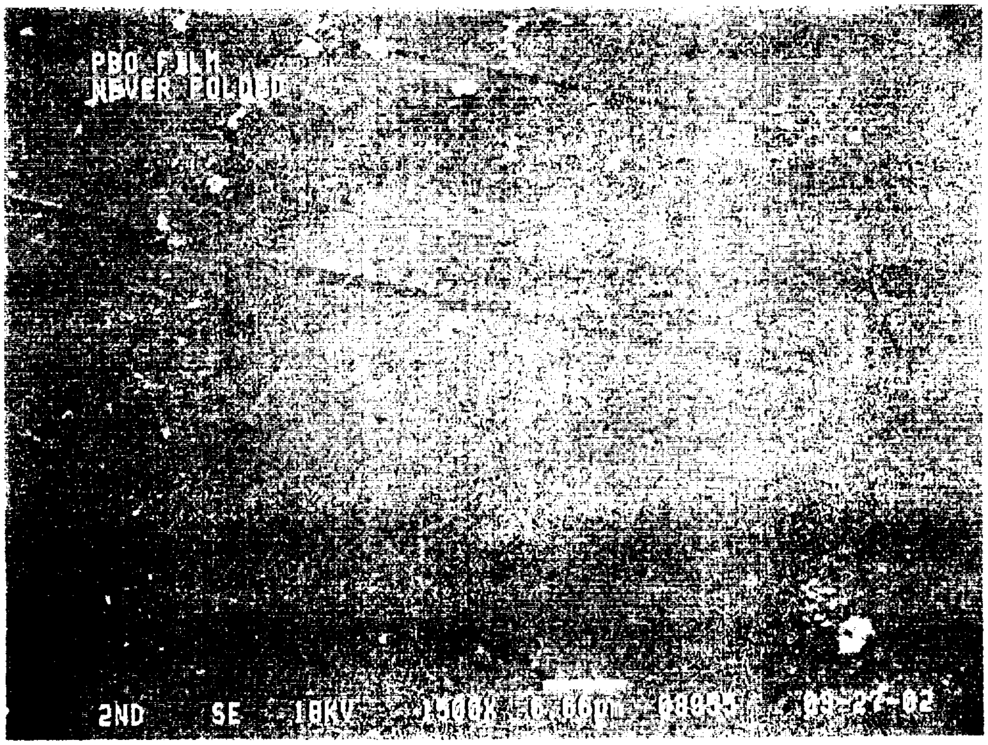


Figure C-1. UTS versus UV exposure

APPENDIX D

SEM MICROGRAPHS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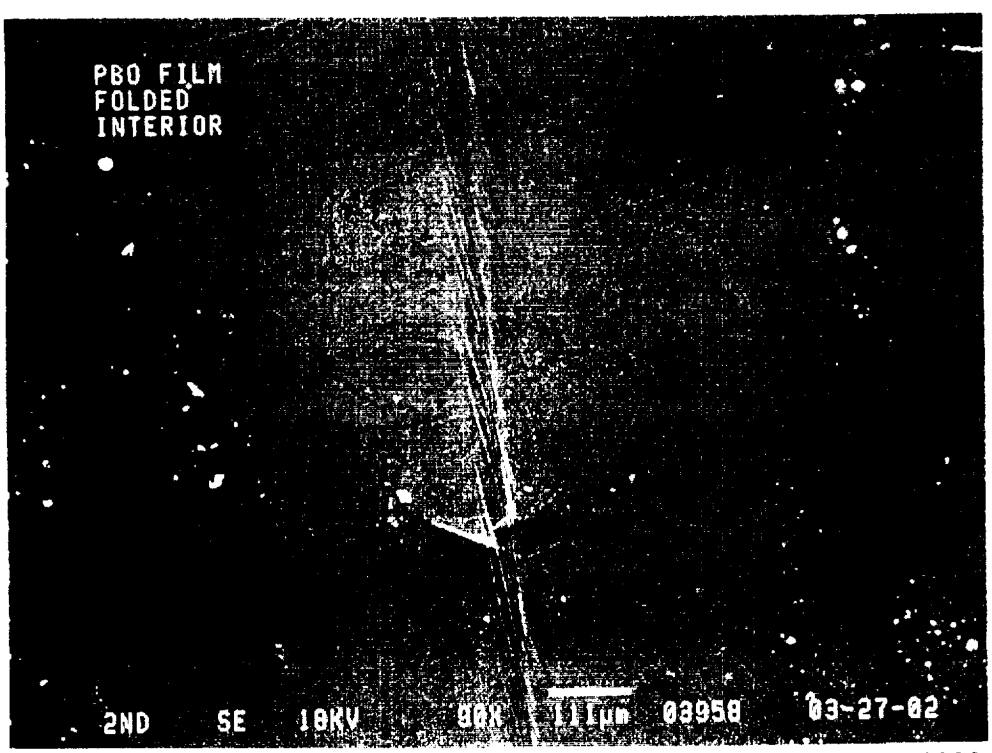
2ND SE 10KV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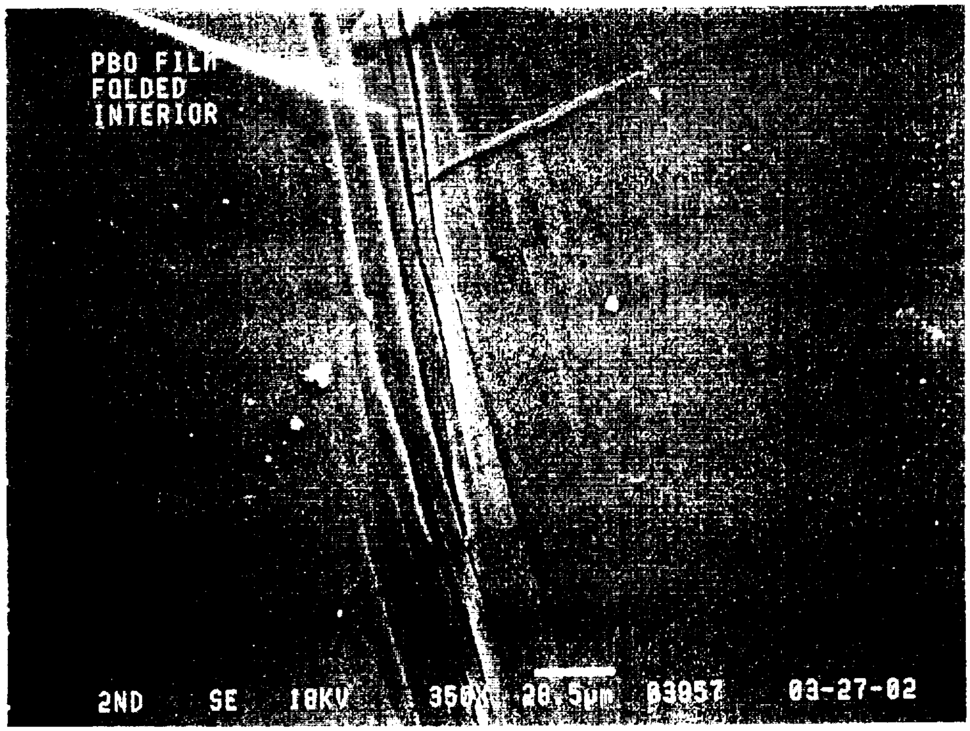
INTERIOR
2ND SE 10KV 03958 03-27-02

02-1902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INTERIOR
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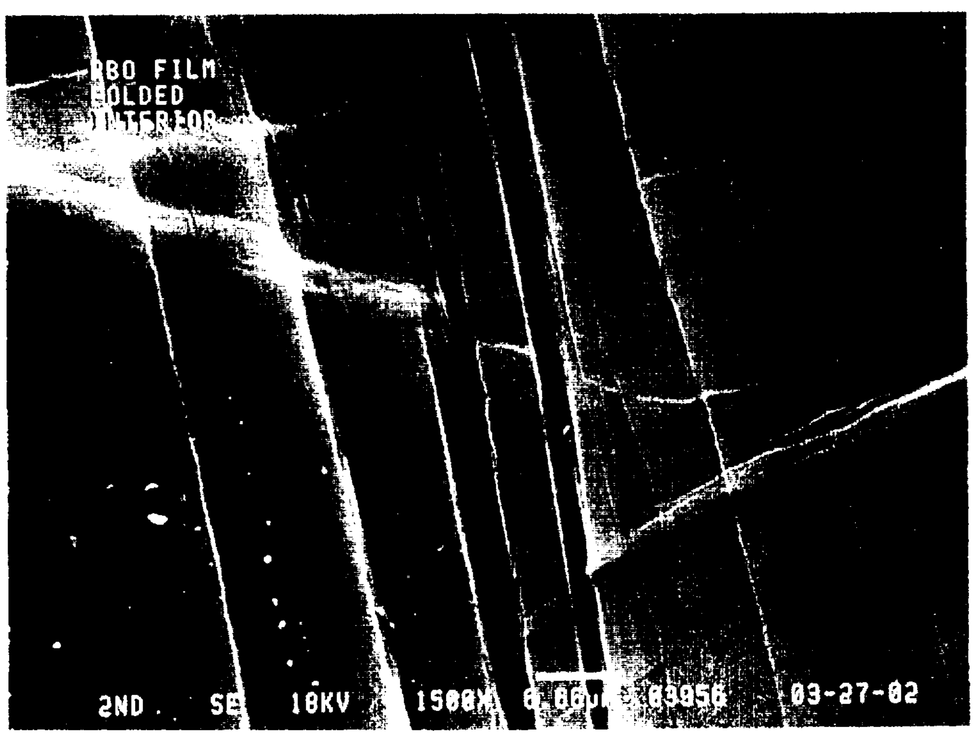
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INTERIOR
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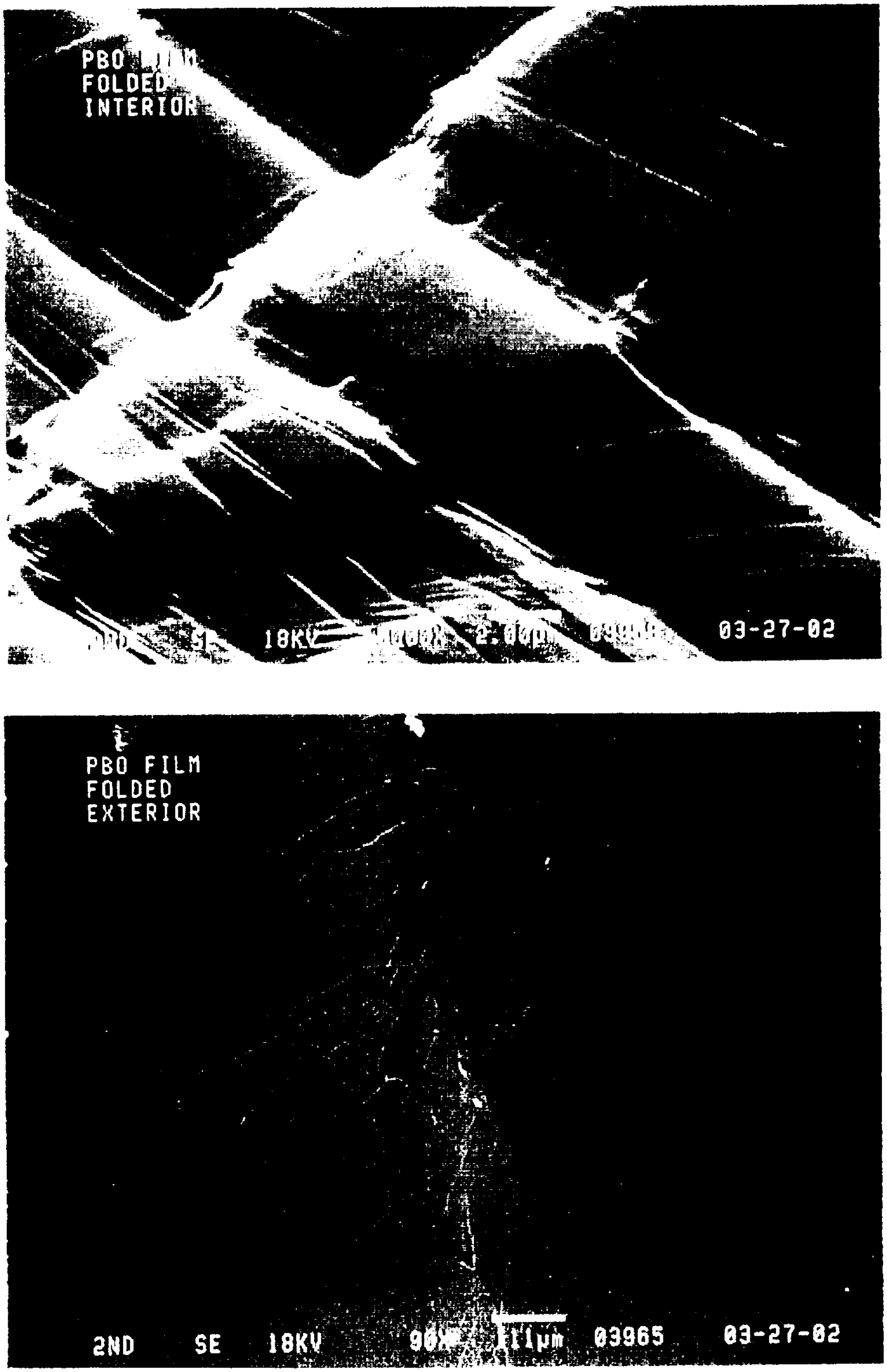
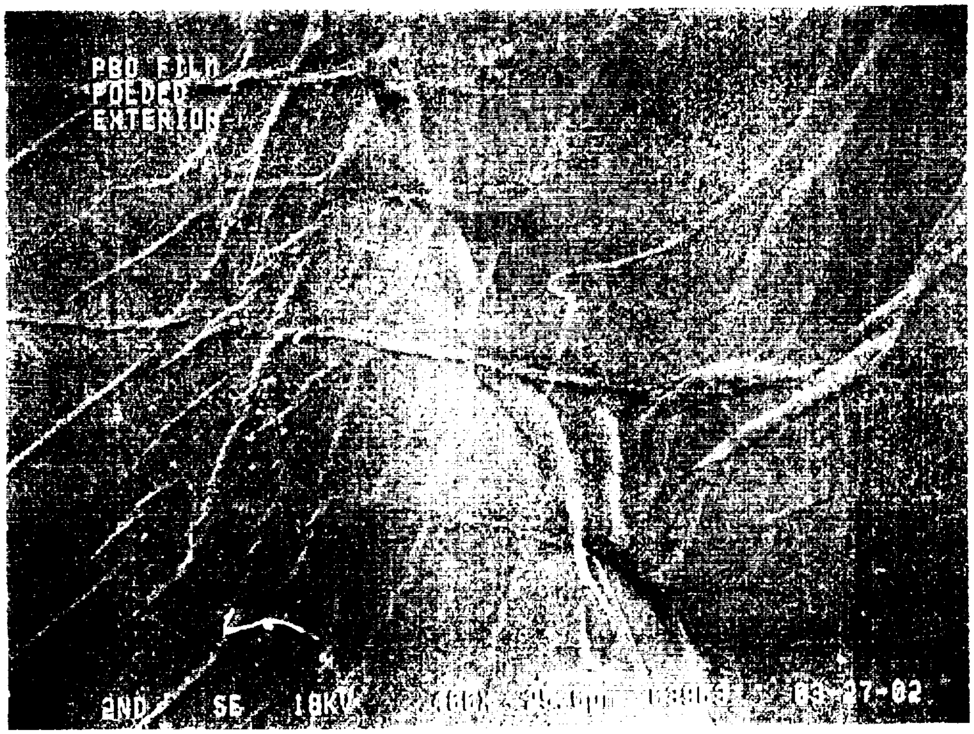
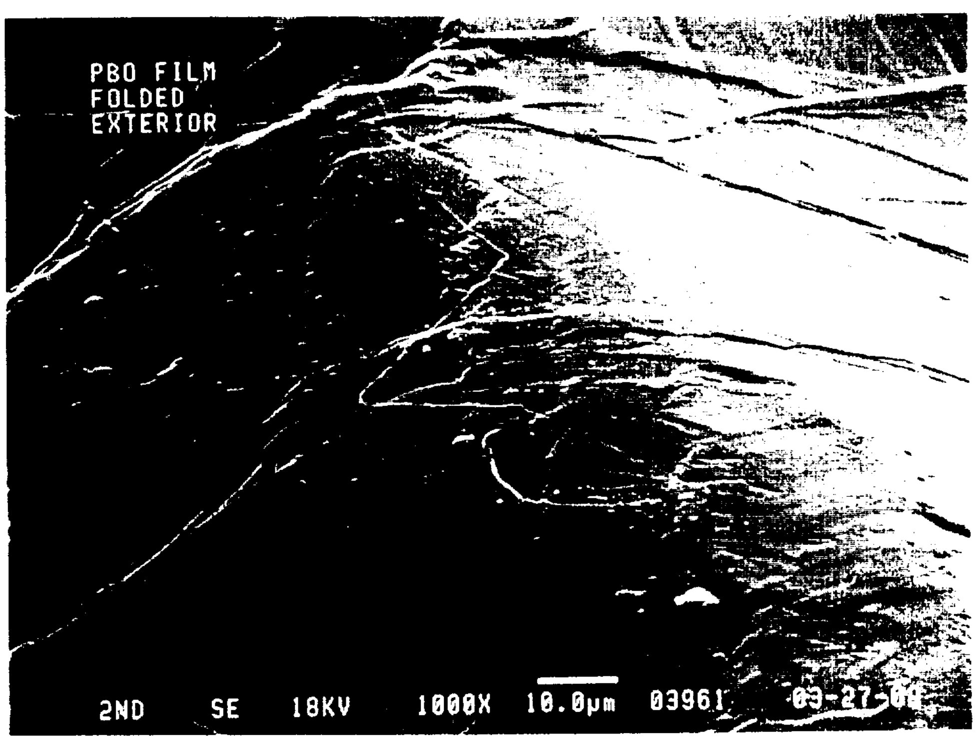
02-1903


PBO
FOLDED
INTERIOR
18KV
03-27-02
PBO FILM
FOLDED
EXTERIOR
2ND SE 18KV 90X 03965 03-27-02

02-1904


PBO FILM
FOLDED
EXTERIOR
2ND SE 18KV
03-27-02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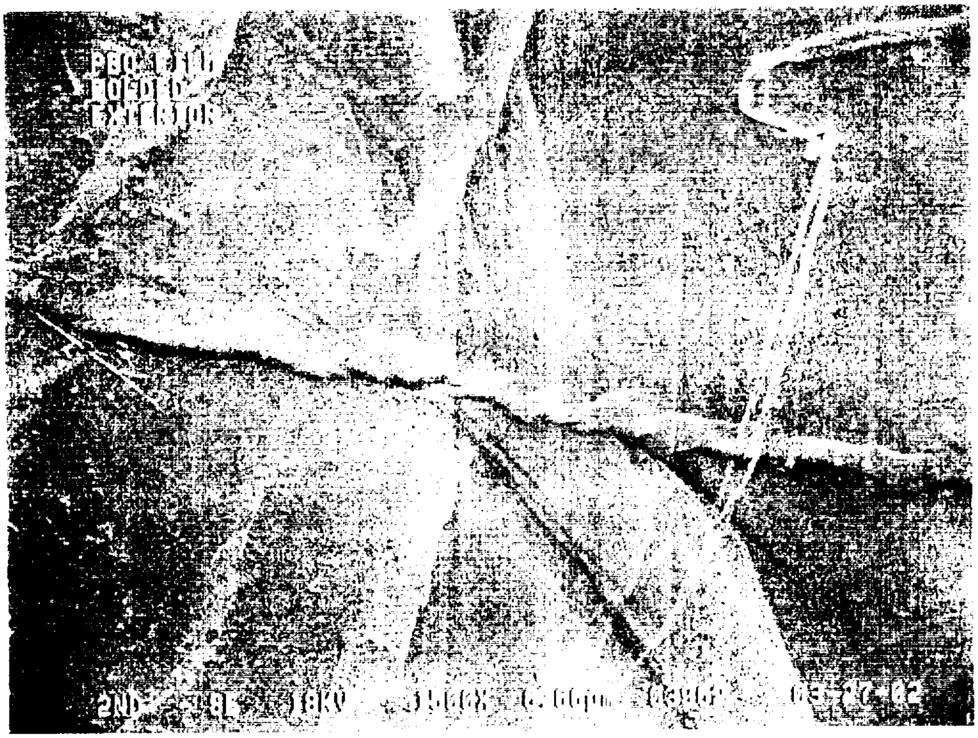
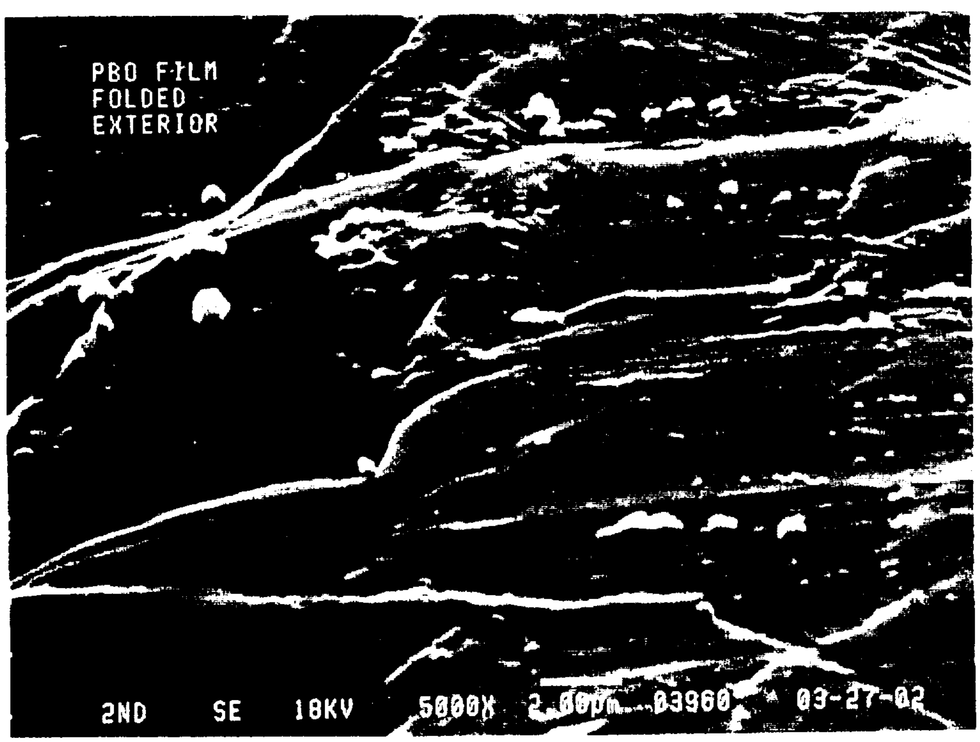
02-1905




PBO FILM
FOLDED
EXTERIOR
2ND SE 18KV 5000X 2.00µm 03960 03-27-02

02-1906

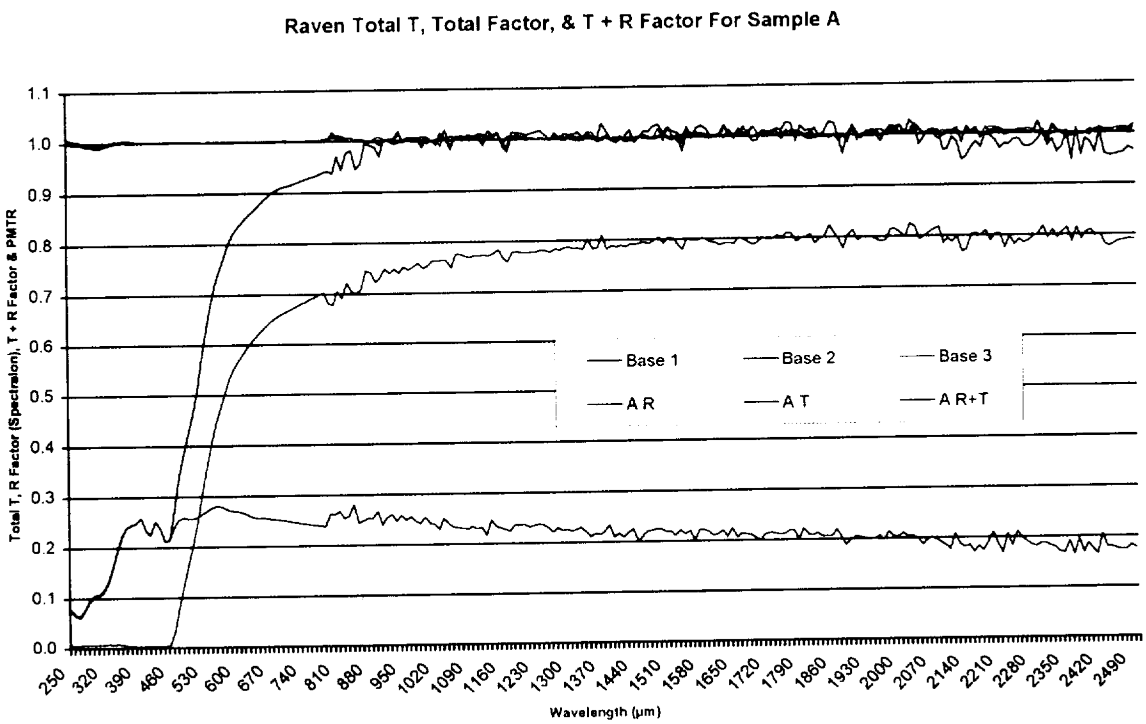
APPENDIX E

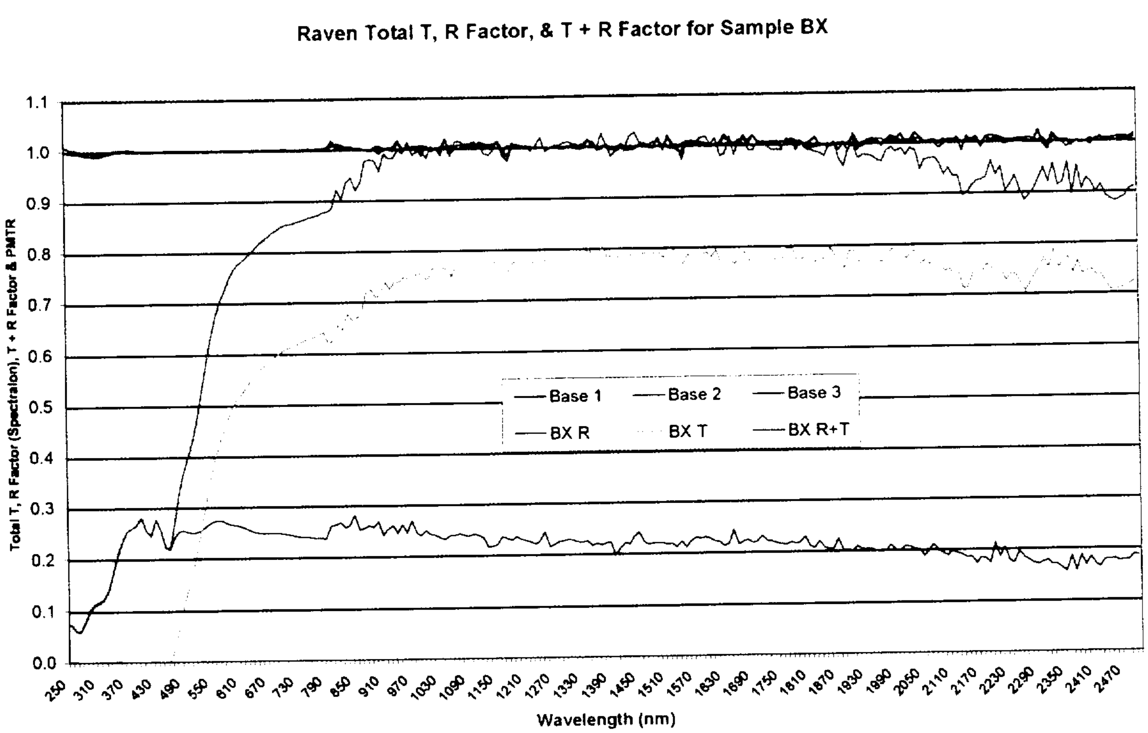
RAVEN OPTICAL RADIATION DATA

E.1 Optical Data Analysis

Optical Data Associates, LLC, tested samples of the PBO material. Two inch square samples, noted as A, BX and C, were used in the tests. Also three samples from the taped area were analyzed in the testing as well. These are noted as AT, BT, and CT. The samples were tested for transmittance (T), reflectance (R) and transflectance (TR). Transmittance is a measure of the fraction of radiant energy that reaches it furthest boundary after entering a layer of absorbing matter. Reflectance is the fraction of total radiant flux incident upon a surface that is reflected and that varies according to the wavelength distribution of the incident radiation.

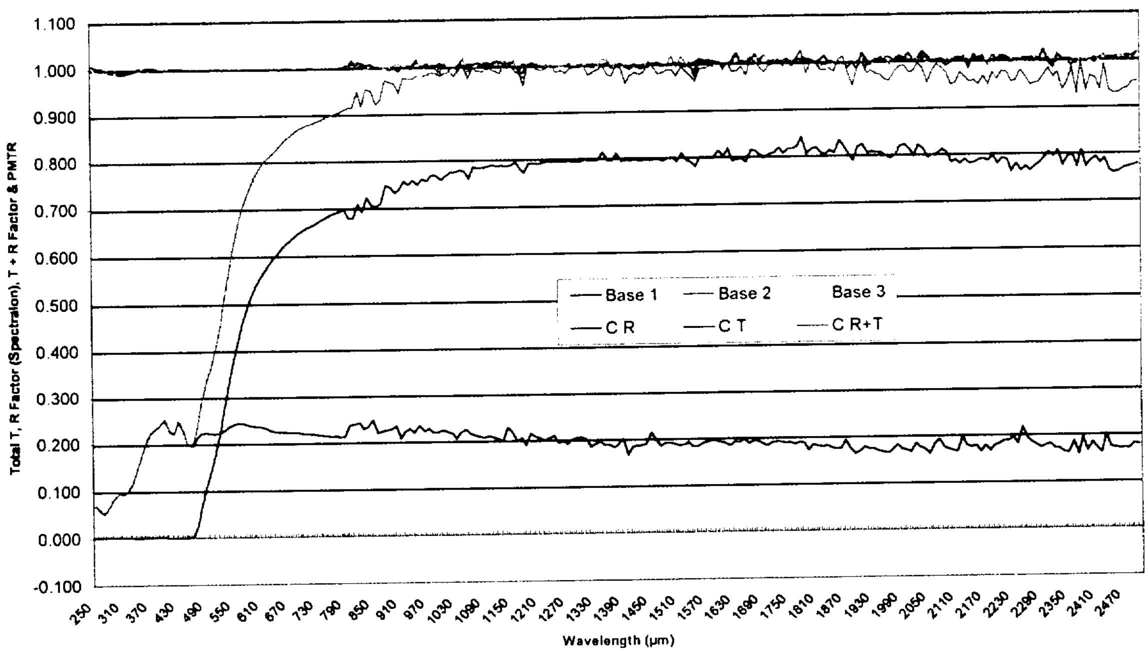
In organic compounds, two bonded atoms are held together by mutual attraction for the shared electron pair that lies between them. The two atoms are free to vibrate back and forth. In addition, the bond axis of one bond may rock back and forth within the plane it shares with another bond or bend back and forth outside that plane. These movements are called bending vibrations. Both stretching and bending vibrations represent different energy levels of a molecule. These energy differences match the energies of wavelengths in the infrared region of the electromagnetic spectrum—i.e., those ranging from 2.5 to 15 μm (μm; 1 μm = 10^{-6}). An infrared spectrophotometer is an instrument that passes infrared light through an organic molecule and produces a spectrum that contains a plot of the amount of light transmitted on the vertical axis against the wavelength of infrared radiation on the horizontal axis. In infrared spectra, the absorption peaks point downward because the vertical axis is the percent transmittance of the radiation through the sample. Absorption of radiation lowers the percent transmittance value.



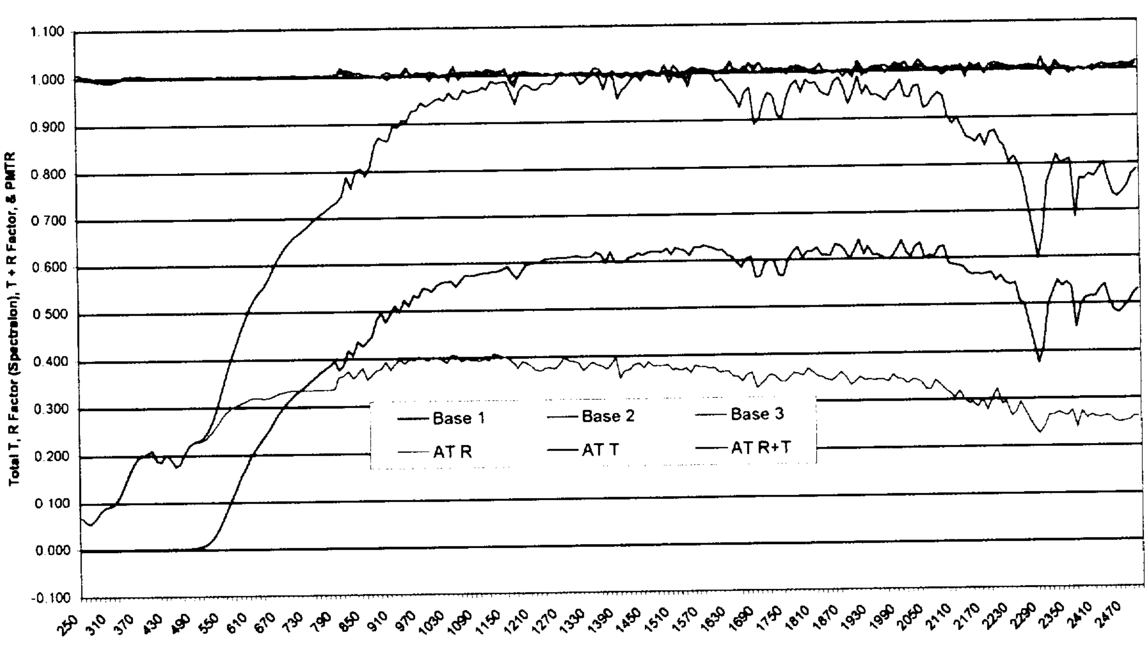


594-DNAS-000067-18

Raven Totoal T, Total R FActor, &T + R Factor for Sample C

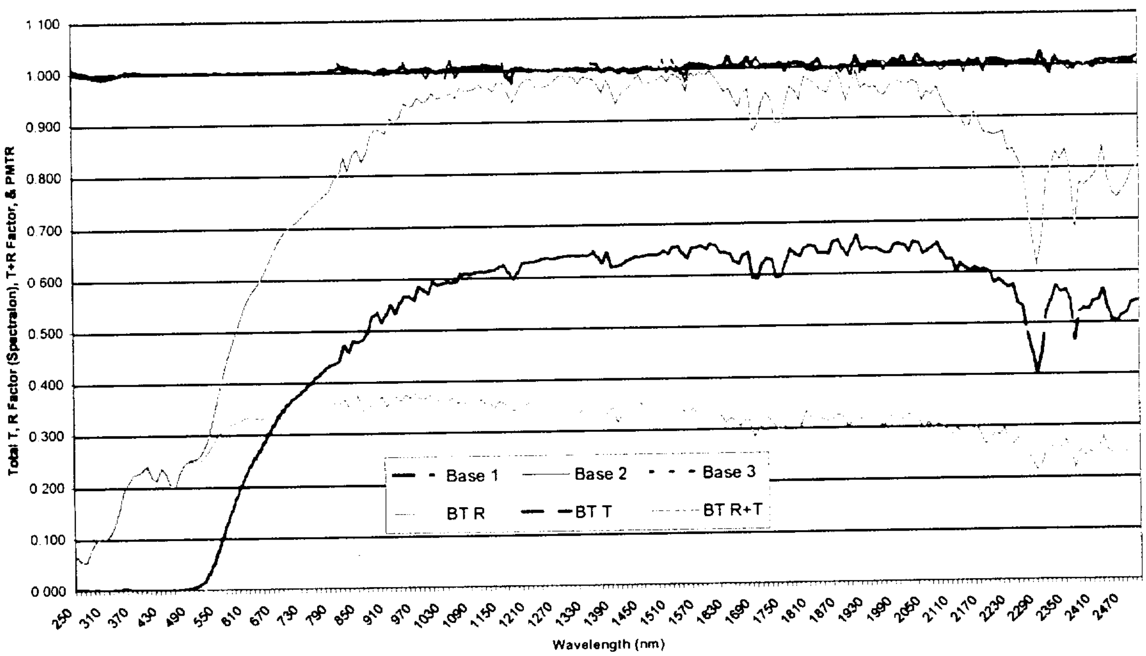


Raven Total T, Total R Factor, & T + R Factor for Sample AT

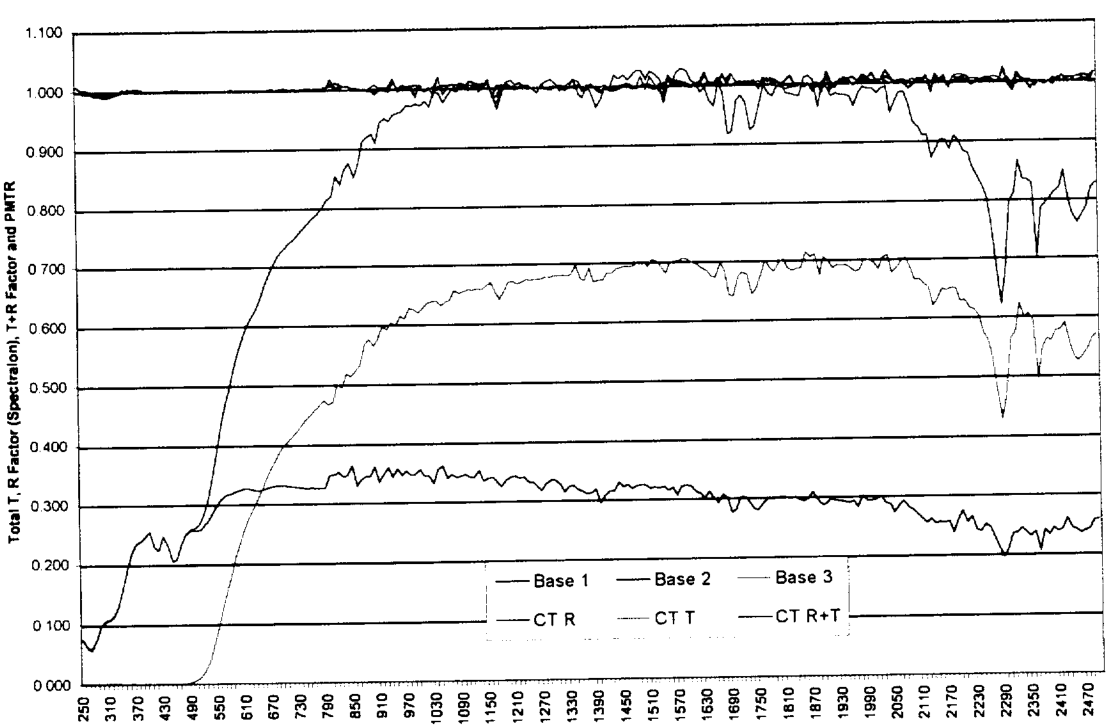


594-DNAS-000067-19

Raven Total T, Totoal R Factor, & T+R Factor for Sample BT

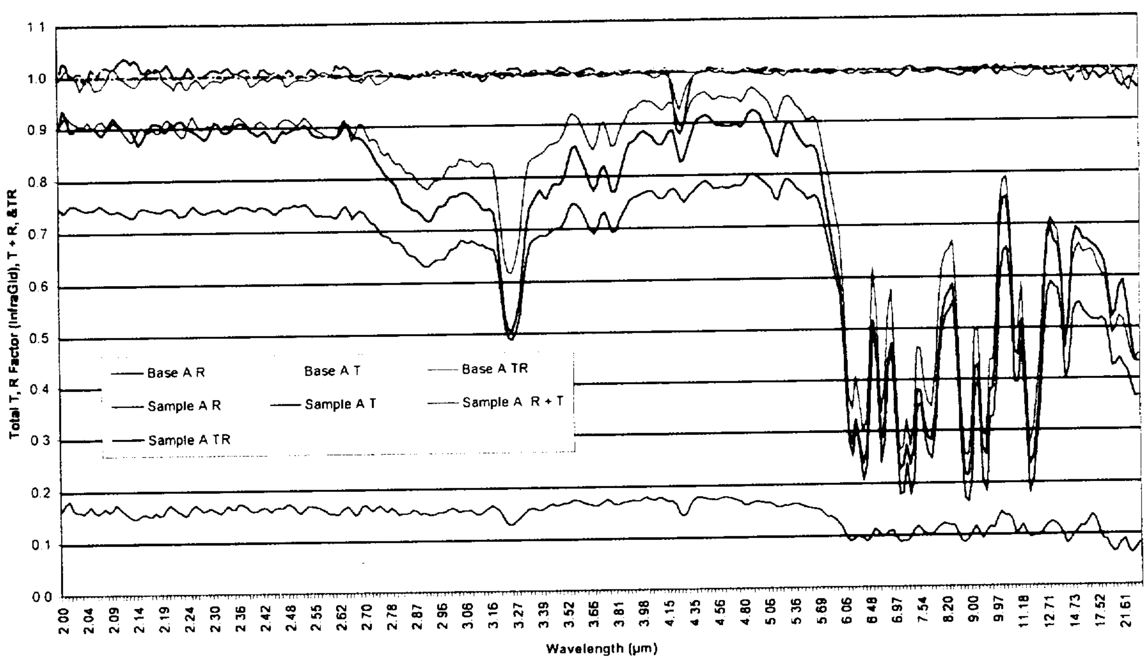


Raven Total T, Total R Factor, T + R Factor for Sample CT

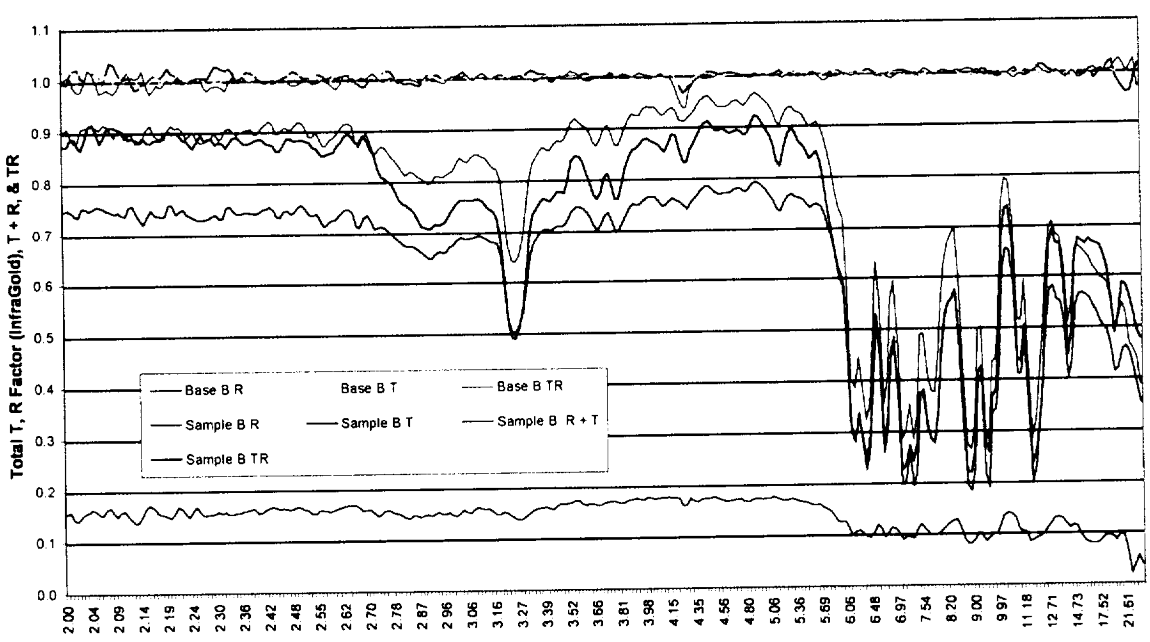


594-DNAS-000067-20

Raven IR Total T, Total R Factor, T+R & TR for Sample A

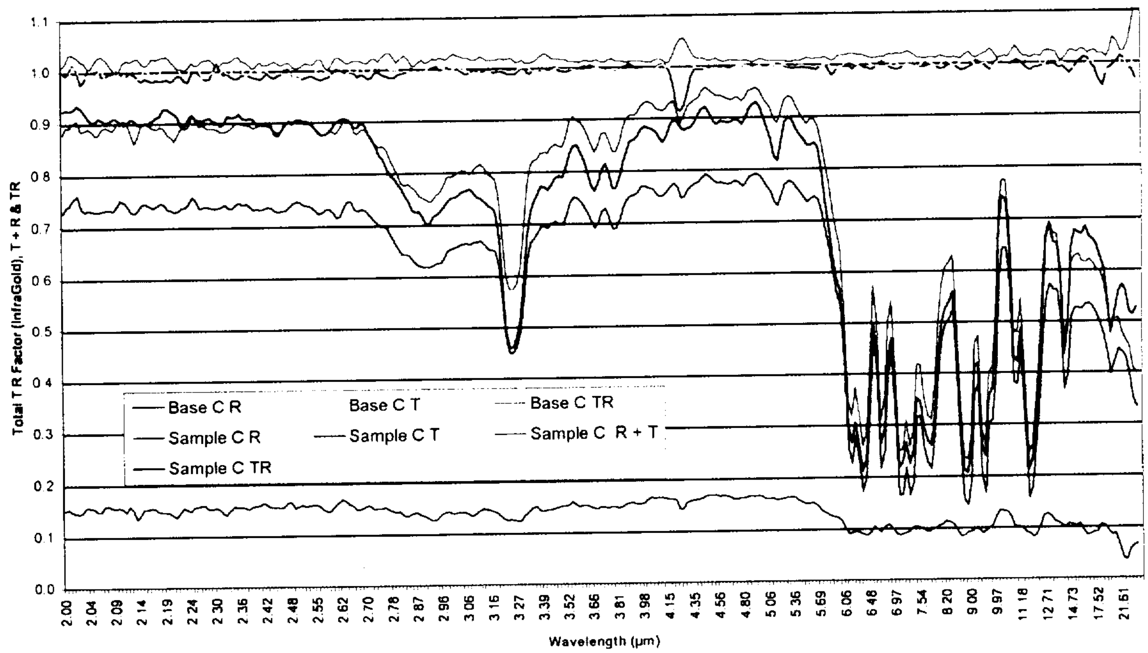


Raven IR Total, Total R Factor, T+R, & TR For Sample B

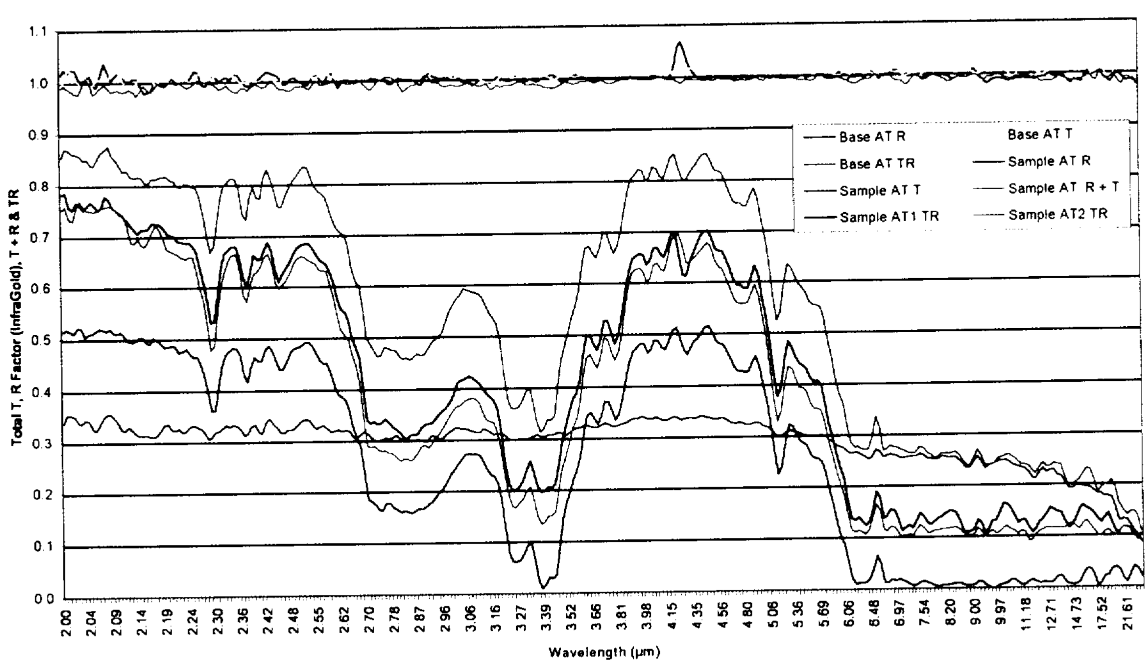


594-DNAS-000067-21

Raven IR Total, Total R Factor, T + R, & TR For Sample C

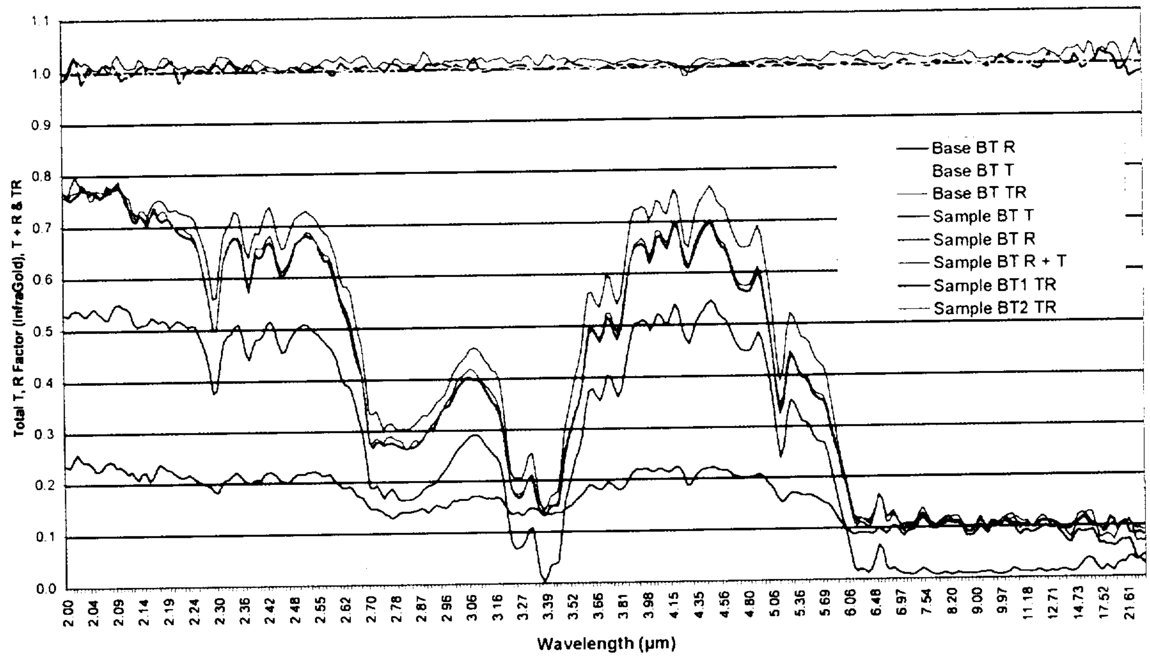


Raven IR Total T, Total R Factor, T+R & TR For Sample AT

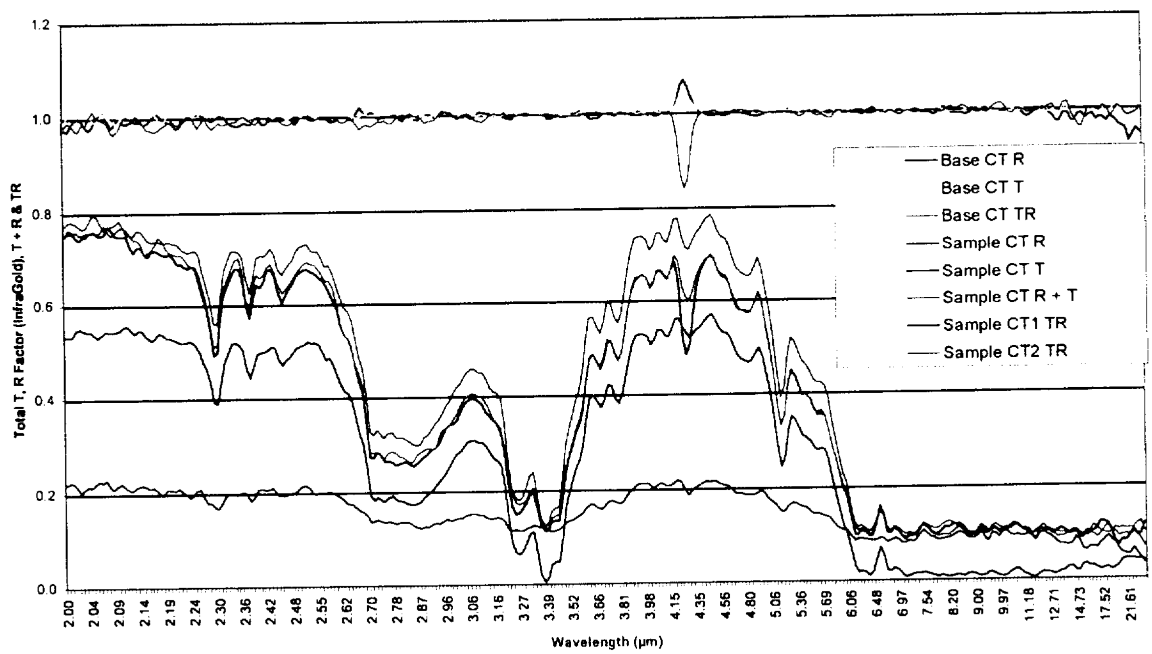


594-DNAS-000067-22

Raven IR Total T, Total R FActor, T + R & TR For Sample BT



Raven IR Total T, Total R Factor, T + R, & TR For Sample CT



594-DNAS-000067-23

Table E-1 contains the solar (Air Mass 1.5) T, R, T+R, derived A = 1 - (T+R) and transflectance data for the Foster Miller PBO material.

Table E-1.

Sample	Solar T	Solar R	Solar T + R	Solar A = (1-R+T)	Solar TR
A	0.573	0.241	0.814	0.186	0.794
BX	0.546	0.242	0.788	0.212	0.794
C	0.571	0.216	0.786	0.214	0.763
AT	0.336	0.320	0.656	0.344	0.630
BT	0.364	0.315	0.679	0.321	0.646
CT	0.397	0.308	0.705	0.295	0.672

As a comparison, Table E-2 contains T, R, T+R and A = 1 = (T+R) for differing thickness of Astrofilm which is commonly used to make scientific balloons.[1] As can be noted from the data, the Foster Miller PBO material has a significantly higher rate of reflectance (R) and a lower rate of transmittance (T).

Table E-2.

Material	Source	Solar T	Solar R	Solar T+R	Solar A
Astrofilm, 0.8 mil	GSFC (1994)	0.9002	0.0764	0.9766	0.0234
Astrofilm, 1.5 mil	GSFC (1994)	0.8216	0.0764	0.8980	0.102
Astrofilm, 2.0 mil	GSFC (1994)	0.7700	0.0764	0.8464	0.1536

Table E-3 contains T, R, T+R, and derived E (emittance) = 1- (T+R) for 20°C.

Table E-3.

Sample	Thermal T	Thermal R	Thermal T+R	Thermal E = 1-T+R	Thermal TR
A	0.450	0.114	0.546	0.436	0.516
BX	0.440	0.128	0.568	0.432	
C	0.431	0.107	0.538	0.462	0.502
AT1/AT2	0.067	0.245/0.232	0.312/0.299	0.688/0.701	0.193/0.169
BT1/BT2	0.073	0.105	.0178	0.822	0.166/0.169
CT1/CT2	0.076	0.100	0.176	0.824	0.163/0.168

[1]Cathey, Henry M., "Advances in the Thermal Analysis of Scientific Balloons," 34th Aerospace Sciences Meeting & Exhibit, January, 1996.

Table E-4 contains T, R, T + R and derived E = 1 - (T+R) at -80°C.

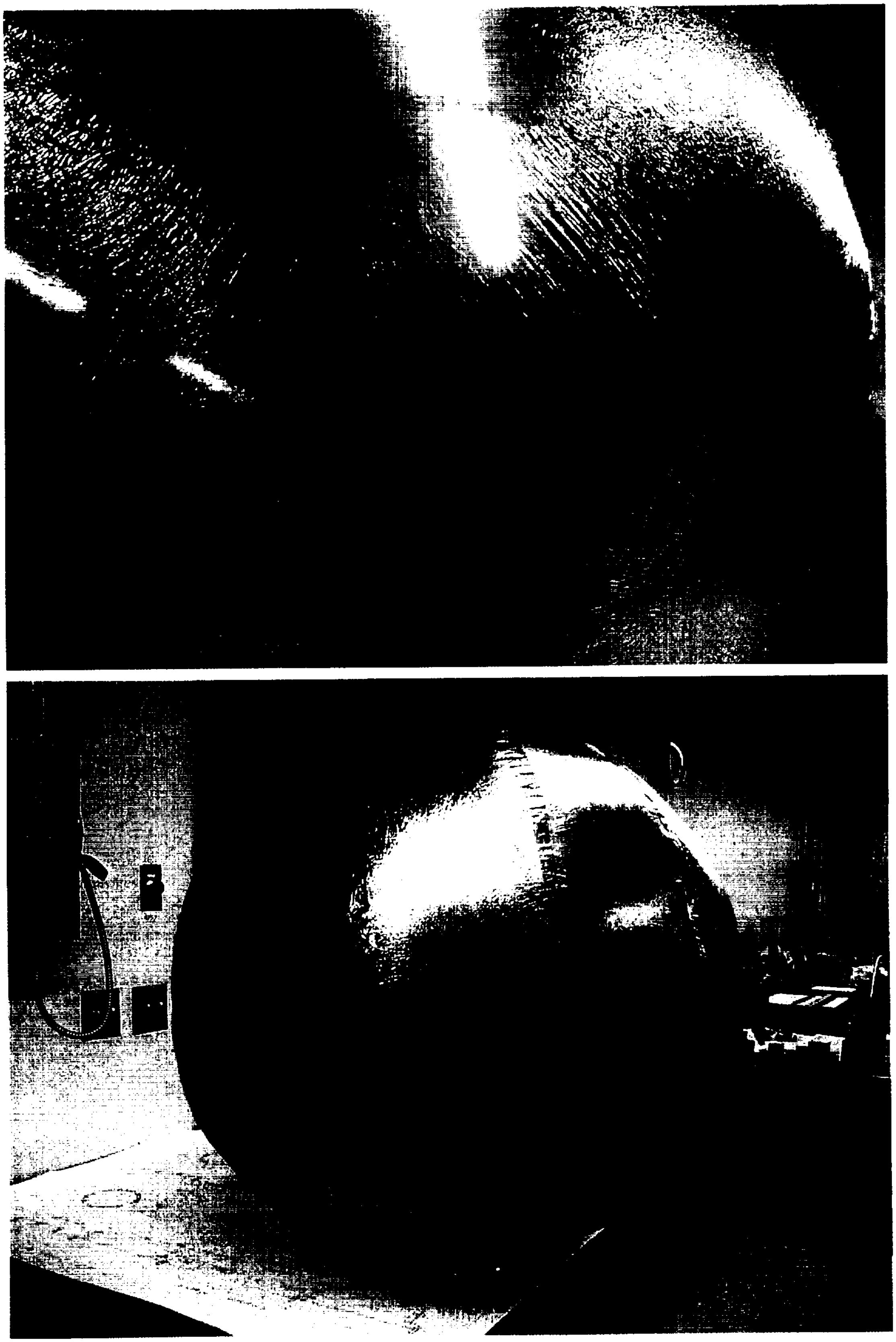
Table E-4.

Sample	Thermal T	Thermal R	Thermal T+R	Thermal E = 1-T+R	Thermal TR
A	0.436	0.103	0.539	0.461	0.519
BX	0.425	0.117	0.542	0.458	
C	0.419	0.096	0.515	0.485	0.507
AT1/AT2	0.019	0.208/0.196	0.227/0.215	0.773/0.785	0.135/0.114
BT1/BT2	0.022	0.085	0.107	0.893	0.106/0.109
CT1/CT2	0.024	0.082	0.106	0.894	0.106/0.110

APPENDIX F

1M BALLOON PHOTOGRAPHS

02-1907



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13. ABSTRACT *(Maximum 200 words)*

During this Phase II program, Foster-Miller scaled up its proprietary blown film extrusion process for producing improved gauge, 22 in. wide biaxially-oriented PBO film suitable for reduced scale aerobot balloon fabrication. Raven Industries, our primary subcontractor, was responsible for balloon analysis, design, fabrication and testing. The results attained from Raven's efforts indicated that planetary aerobots fabricated from PBO film can meet or exceed many of NASA's rigorous requirements for an extraterrestrial balloon.

The PBO film produced and used in this program, however, exhibited two deficiencies that will need to be corrected to make this product an optimal extraterrestrial balloon envelope material. Firstly, PBO film when exposed to UV and/or visible light for extended periods of time can lose up to 60 to 65 percent of its mechanical strength. Research in this area, conducted by Foster-Miller and Toyobo, the manufacturer of PBO fiber (Zylon), has demonstrated that thin (μm thick) coatings (silicon oxide or fluorocarbon based) can significantly mitigate this problem. The second property that needs to be addressed is the gauge uniformity (thickness consistency) of the film. Analysis has indicated that a maximum gauge deviation of ±10 percent is a reasonable target for obtaining the desired strength to weight ratio and burst safety factor for the balloon envelope material. During this program the best gauge uniformity achieved was ±19.5 percent.

Two spherical 1.5m PBO flight balloons were delivered to NASA for evaluation. Raven retained a 1m balloon and tested it for burst strength after fabrication. The balloon was pressurized to 0.92 psi before bursting. This translates to a stress of 72 ksi (at the measured thickness of 0.12 mil) at the point of failure.

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